MANUAL FOR TESTING OF WATER AND WASTEWATER TREATMENT CHEMICALS

Final report

prepared for the

Water Research Commission

by

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Executive Summary

A large number of chemicals are used in the production of potable water and in the treatment of wastewater effluents. In potable water treatment chemicals such as inorganic salts and polymeric organic coagulants are used for primary coagulation, as coagulant aids and for sludge dewatering; lime and soda ash allow for pH correction and water stabilisation; caustic soda is used for pH adjustment; powdered activated carbon (PAC) can remove taste and odour compounds and micropollutants such as atrazine; bentonite aids coagulation; and ammonium hydroxide is used in chloramination.

Wastewater treatment is generally performed using a predominantly biological process in South Africa, but here too chemicals are often used, such as coagulants for sludge conditioning, lime for pH adjustment and to increase the alkalinity content, and aluminium and iron salts for phosphate removal.

However, standardised testing procedures for assessing these process chemicals are seriously lacking in this country. There are some recommended tests available for the assessment of some of these chemicals, such as the South African Bureau of Standards 459-1955 Standard Specification for Lime for Metallurgical Purposes, but the tests described in this specification are for the most part outdated gravimetric procedures which are time consuming.

In the case of polyelectrolytes used for primary coagulation in potable water treatment, there is currently no legislation or regulation system present in this country for the control of these chemicals and no standard tests are available to measure the effectiveness of these chemicals for coagulation. Prior to 1994 all suppliers needed to supply Department of Health certification before their products would be considered for use by UW, but this certification appears to have been issued on an ad hoc basis, subject to the supplier being able to supply approval or certification for his product or the monomer/s from a recognised world health body such as the World Health Organisation (WHO), the United States Environmental Protection Agency (USEPA) and the European Economic Community (EEC). After 1994 the issuing of such certification by the Department of Health fell away altogether. Water utilities such as Umgeni Water insist that recognised certification is supplied by the polyelectrolyte

supplier before using his product, but this system is considered inadequate since it lacks uniformity. The Department of Health is presently in the process of implementing a regulatory system for polyelectrolyte control, but this is not expected to be functional for some time yet.

Similar problems are experienced with sludge treatment coagulants, since tests available for the assessment of these polyelectrolytes don't necessarily adequately describe the performance of these chemicals for dewatering. At present, no national standard for testing these chemicals exists.

Problems also arise in assessing powdered activated carbon (PAC). A number of tests are available to measure various parameters such as iodine number, methylene blue number, phenol number and molasses number. Bodies such as the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM) and the Council of Chemical Manufacturers' Federations (CEFIC) have standard procedures for conducting such tests, but at present there is no uniformity in South Africa regarding the test procedures used. For example there are three different phenol tests available (Chemviron Carbon, 1998), the most commonly used being the German Standard DIN19603 (1969). There are also two AWWA methods, one for PAC and another for granular activated carbon (GAC). The same is true for iodine number and methylene blue number, at least two or three standard tests being available in each case.

In addition to this, these parameters, although useful for production quality control, are not particularly effective for assessing the operating performance of the carbon in terms of micropollutant removal (Chemviron Carbon, 1998). In the experience of the authors, a low iodine number generally indicates that the carbon will not be effective for taste and odour removal, but a high iodine number gives no indication of the ability of the carbon to adsorb these micropollutants. Since micropollutant removal is the usual application of activated carbon in water treatment, it has been necessary for a number of Southern African Water Authorities to devise an alternative method for assessing this parameter.

The lack of any standardised testing procedures makes it difficult to assess or compare these products, or to conduct routine quality control tests on them, which could even result in negative health and environmental implications. There are also

no standard procedures available for conducting tender evaluations of these chemicals. Therefore Umgeni Water, in conjunction with the Water Research Commission, undertook to collate and evaluate the various test procedures available for assessment of the most commonly used chemicals in the water and wastewater treatment industries, resulting in the production of this manual. The manual attempts to address a number of these inadequacies and contains standard tests, many of which can be conducted using relatively simple equipment, procedures for evaluation of process chemicals, standard worksheets for the various tests as well as spreadsheets for those tests requiring calculations.

i.i Objectives

There were three main objectives of this project:

1. Assess the various procedures used in Southern Africa to evaluate the different chemicals used in water and wastewater treatment.

2. Identify the critical determinands for evaluation of water and wastewater treatment chemicals and recommend standard procedures for testing these.

3. Produce a manual for all Southern African water and wastewater authorities to use for evaluation of the chemicals used in water and wastewater treatment. This manual would set out standard procedures for the assessment of water and wastewater treatment chemicals and wherever possible, these procedures would be simple enough that they could be performed without the need for sophisticated instrumentation.

i.ii Methodology

Initially a literature survey was conducted in order to gather all available test procedures for the following water and wastewater treatment chemicals:

polyelectrolytes for primary coagulation and as coagulant aids
polyelectrolytes for sludge dewatering
bentonite
inorganic coagulants (e.g. aluminium sulphate, ferric chloride)
lime (quicklime and slaked lime)
soda ash

caustic soda
oxidants and disinfectants (e.g. hypochlorite, chlorine dioxide, ozone, hydrogen peroxide, bromine)
ammonium hydroxide
activated carbon
fluoride

Once this had been done, a number of the main role players in the water and wastewater industry in Southern Africa were consulted regarding the test procedures which they use. Institutions, water authorities and companies which collaborated with the authors by providing test procedures, information and chemicals are listed below:

Rand Water
City of Cape Town
Nelson Mandela Metropolitan Council
BHT-Sudchemie
Zetachem

Most of the tests were evaluated in the Research and Development Laboratories, Umgeni Water to determine their accuracy, repeatability, limit of detection and the ease with which each test could be performed and its value in assessing a particular chemical. Emphasis was placed in selecting tests that not only analysed critical factors for a treatment chemical, but which were both accurate and simple wherever possible. Whenever a test required sophisticated instrumentation, attempts have been made to provide an alternative that can be conducted using simpler technology.

i.iii Summary of Manual

This manual is divided into 9 chapters, the first being an introduction and the last containing reference details, while Chapters 2 to 8 deal with test procedures for logical groupings of water and wastewater treatment chemicals, these being:

Chapter 2: Coagulants
Chapter 3: Coagulant Aids
Chapter 4: Sludge Treatment Coagulants
Chapter 5: pH Adjustment and Stabilisation Chemicals
Chapter 6: Oxidants and Disinfectants
Chapter 7: Activated Carbon
Chapter 8: Fluoridation Chemicals

Where relevant worksheets have been included at the end of a section or method to assist the user in entering the necessary data and carrying out calculations.

The methods contained in the manual have been taken from a wide variety of sources including Standard Methods for the Examination of Water and Wastewater, the America Water Works Association (the ANSI/AWWA methods), the American Society for Testing and Materials (ASTM), the Council of Chemical Manufacturers' Federations (CEFIC), the German Standard DIN Standards as well as tried and tested methods from the Umgeni Water Laboratories and from the collaborators mentioned in Section i.ii above.

This has resulted in a manual that provides testing procedures for most of the chemicals used in water and wastewater treatment in Southern Africa, that are generally fairly simple to conduct and which are reliable and repeatable. It is hoped that this manual will offer the first step towards providing standardised procedures for the evaluation of water and wastewater treatment chemicals and assist in providing the technical background for future legislation governing the use of these chemicals.

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Abbreviations and Glossary

Alum	Aluminium sulphate
ASDWA	The Association of State Drinking Water Administrators
AWWA	American Water Works Association
AWWARF	American Water Works Association Research Foundation
COSHEM	Conference of State Health and Environmental Managers
DPD	Diethyl phenylenediamine
EEC	European Economic Community
EU	European Union
$FeCl_3$	Ferric chloride
$Fe_2(SO_4)_3$	Ferric sulphate
GAC	Granular activated carbon
MAL	Maximum allowable limit
MCL	Maximum contaminant level
NSF	National Sanitation Foundation
PAC	Powdered activated carbon
RG	Reagent grade
SANAS	South African National Accreditation Services
SABS	South African Bureau of Standards
USEPA	United States Environmental Protection Agency
UV	Ultraviolet irradiation
WHO	World Health Organisation
WW	Water Works
WWW	Wastewater Works

1. INTRODUCTION

A large number of chemicals are used in the production of potable water and in the treatment of wastewater effluents. In potable water treatment, chemicals such as inorganic salts and polymeric organic coagulants are used for primary coagulation, as coagulant aids and for sludge dewatering; lime and soda ash allow for pH correction and water stabilisation; caustic soda is used for pH adjustment; powdered activated carbon (PAC[11]) can remove taste and odour compounds and micropollutants such as atrazine; bentonite aids coagulation; and ammonium hydroxide is used in chloramination.

In this country wastewater treatment is generally performed using a predominantly biological process, but here too chemicals are often used, such as coagulants for sludge conditioning, lime for pH adjustment and to increase the alkalinity content, and aluminium and iron salts for phosphate removal

At present there are tests available for the assessment of some of these chemicals such as the SABS 459-1955 Standard Specification for Lime for Chemical and Metallurgical Purposes. However, the tests described in this specification are for the most part outdated gravimetric procedures, which are particularly time consuming.

In the case of polyelectrolytes used for primary coagulation during potable water treatment, there is currently no legislation or regulation system in this country to control the use of these chemicals and no standard tests are available to measure the effectiveness of these chemicals for coagulation. Tests available for assessment of polyelectrolytes used for sludge treatment don't necessarily describe adequately the performance of these chemicals for dewatering.

Problems also arise in assessing PAC. A number of tests are available to measure various parameters such as iodine number, methylene blue number, phenol number and molasses number. Bodies such as the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM) and the Council of

[1] PAC can also be used as an abbreviation for polyaluminium chloride, but for the purposes of this manual, PACl will be used as an abbreviation for polyaluminium chloride.

Chemical Manufacturers' Federations (CEFIC) have standard procedures for conducting such tests, but at present there is no uniformity in South Africa regarding the test procedures that should be used. For example there are three different phenol tests available, the most commonly used being the German Standard DIN19603 (1969). There are also two AWWA methods, one for PAC and another for granular activated carbon. The same is true for iodine number and methylene blue number, with at least two or three standard tests being available in each case.

In addition to this, these parameters, although useful for production quality control, are not suitable for assessing the operating performance of the carbon (Chemviron Carbon). In the experience of Umgeni Water, a low iodine number generally indicates that the carbon will not be effective for taste and odour removal, but a high iodine number gives no indication of the ability of the carbon to adsorb these micropollutants. Since micropollutant removal is the usual application of activated carbon in water treatment, it has been necessary for Umgeni Water, as well as a number of other Southern African Water Authorities, to devise a method for assessing this.

The lack of standard tests in the water and wastewater chemical industry make it difficult to assess or compare chemicals, or to conduct routine quality control tests on them and this can have negative health and environmental implications. There are also no standard procedures available for conducting tender evaluations of these chemicals. This handbook attempts to address a number of these inadequacies and contains standard tests, many of which can be conducted using relatively simple equipment, procedures for evaluation of process chemicals, standard worksheets for the various tests as well as spreadsheets for those tests requiring calculations.

2. COAGULANTS

2.1. INTRODUCTION

Coagulation is an important part of conventional water treatment. It is the process in which negatively charged particles present in water in a stable suspension are destabilised by the addition of coagulant (positively charged), which allows for aggregation of the particles. Sedimentation, followed by filtration then bring about the removal of the aggregated particles.

A coagulant is any chemical that is used to bring about the agglomeration of colloidal particles and a wide range of such chemicals exist. They can be classified as inorganic or mineral compounds such as aluminium sulphate and ferric chloride or as organic, such as polyelectrolytes.

Inorganic or mineral coagulants, such as aluminium sulphate have been used for the coagulation of colloidal suspension in water for centuries, while in comparison, polyelectrolytes are a relatively new innovation in water treatment. Polyelectrolytes are used in water treatment both for coagulation and as coagulant/flocculant aids to strengthen flocs and improve their settleability (van Duuren, 1997). The choice of coagulant depends on the chemical requirements of the treatment process. For waters containing a high degree of humic substances (e.g. highly coloured waters) as well as clay particles, inorganic coagulants generally perform better, since metal salt–humic complex formation occurs first and these compounds in turn neutralise the charge and serve as bridging precipitates for the clay colloids (van Duuren, 1997). Positively charged polyelectrolytes, which are of much higher molecular weights (around 10^5) than the inorganic coagulants, are effective on many types of raw water where they act as the neutralising and bridging agent at the same time. However, they are not effective for the coagulation of colour particles (Tambo, 1990). Weakly charged anionic or non-ionic polyelectrolytes of even higher molecular weights (10^6 to 10^7) are used as coagulants aids, to strengthen and improve the settlability of flocs formed using inorganic coagulants (Tambo, 1990).

2.2. INORGANIC COAGULANTS

In theory one could use any of a number of divalent or trivalent metal ions to neutralize the surface charges of the particles suspended in the water and coagulate them. By selecting metals with very sparingly soluble hydroxides, sulphates or carbonates, one can also obtain the bridging flocculation process as well with the addition of a single chemical. In practice however, for obvious reasons only metal salts which are common, relatively inexpensive and effective, are used.

2.2.1. ALUMINIUM SULPHATE

Aluminium sulphate or alum has been used for several centuries in water treatment and is probably the most well known and commonly used coagulant. The chemical is prepared by reacting bauxite or certain clays with sulphuric acid. If the transportation distance is not too great the reacted solution can be taken to the waterworks and used directly. Alternatively the solution can be concentrated by evaporation and crystallized to the solid form and delivered as lumps (kibbles) or ground and delivered in granular or powder form.

Aluminium sulphate is often known as alum (although it is not a true alum) and is acidic in nature. Its storage and handling requires corrosion-proof tanks, pumps and pipework. Aluminium sulphate when delivered in solution form is usually about 48% strength as $Al_2(SO_4)_3.14H_2O$ (including by convention the waters of hydration) and has a specific gravity (SG) of about 1,33 at normal temperatures. Stronger solutions tend to crystallize at low temperatures. The measurement of the SG of an alum solution is a rapid check on its strength and is often used to check consignments before doing a full analysis.

Alum when prepared from virgin chemicals does not normally contain any impurities of concern. Pure alum is white and gives a water-white solution. However the presence of iron as an impurity is common which gives the chemical or the solution a yellow or even an orange colour. Iron is not a problem as an impurity as it is a coagulant in its own right and tends to assist the coagulation process. Alum is sometimes prepared from low-grade clays and from waste acid. This in some cases leads to the presence of undesirable concentrations of heavy (toxic) metals in the solution. Although the alum is usually much cheaper in such cases care should be

taken when approving its use and it is probably better to confine the use of low grade alum to wastewater treatment.

2.2.2. FERRIC CHLORIDE

Ferric chloride, as is the case for the other iron salts, was originally a waste product from spent pickling solution. However, now that demand has increased it is purpose made. It is readily prepared from reacting scrap iron with hydrochloric acid. Because it is highly deliquescent in its crystalline form it is almost invariably supplied as a solution. Ferric chloride is highly acidic and the solution contains free hydrochloric acid. The solution is highly corrosive to nearly all normally used metals including all grades of stainless steel and needs to be stored, pumped and conveyed in synthetic corrosion-resistant materials. The chemical is normally supplied as a solution of about 40% strength as $FeCl_3$ with an SG of about 1,4 and a pH of less than 1.

2.2.3. FERRIC SULPHATE

Ferric sulphate is normally not cost competitive for water treatment, but its use is known. It has been used in wastewater treatment in this country where it has been prepared from waste chemicals. It is also corrosive and has a low pH although it is more comparable in this regard to aluminium sulphate solutions. Although it can be supplied in solid form it is usually supplied as a solution. The strength of solution supplied is not fixed by convention as much as for the other chemicals. The purchase of ferric sulphate (or ferric chloride) is therefore often based on its iron content as Fe. Depending on solution strength this may range from about 8% up to 14%.

2.2.4. FERROUS SULPHATE

Ferrous sulphate is seldom used in water treatment as it needs to be used in conjunction with lime or chlorine to precipitate the iron hydroxide in ferric form. There is however no theoretical reason why it should not be used provided the chemical is cost competitive on the basis of iron content and it does not contain other heavy metals in appreciable quantities.

2.2.5. LIME

Lime is the exception to the almost exclusive use of aluminium and ferric salts for coagulation. The addition of hydrated or slaked lime to water to raise the pH to above 10,5 to 11,5 causes initial floc formation of magnesium hydroxide if dolomitic lime is used. Recarbonation of the water with carbon dioxide to about pH 8 then precipitates

the calcium present (including the calcium bicarbonate originally present in the water) as the carbonate, thereby forming a floc. This process therefore softens the water and removes heavy metals such as manganese as well as the suspended matter originally present in the water. When lime is used in large quantities such as for this process, it is sometimes cheaper to purchase calcium carbonate and to calcine it in ones own limekilns and to use the carbon dioxide generated when producing the quicklime for the recarbonation process. Alternatively quicklime can be purchased and slaked on site and liquid carbon dioxide purchased for the recarbonation.

2.3. POLYELECTROLYTES

The polyelectrolytes used in water treatment are high molecular weight, synthetic organic polymers, produced by the polymerisation of one (homopolymer) or more (copolymer) types of monomer units. Since the type and number of monomer units can be varied during the manufacture of polyelectrolytes, a wide variety of polymers can be produced. In addition to this the polymer chains can be linear, branched or cross-linked, adding to their complexity (Letterman and Pero, 1990).

The molecular weight, solubility and electronic charge can provide useful information regarding the efficacy and the toxicity of a particular polymer (Nabholz et al, 1993). Polymers can contain both negatively and positively charged sites and are usually classified according to this, cationic having an overall positive charge, anionic an overall negative charge, non-ionic being neutral and amphoteric having both positive and negative sites (Letterman and Pero, 1990; Hamilton et al, 1994). The more highly charged a polymer, the more soluble it is likely to be and therefore also the more bioavailable to aquatic organisms (Hamilton et al, 1994). Cationic polyelectrolytes are usually referred to as primary coagulants, while non-ionic and anionic are referred to as coagulant aids or flocculants and these have relatively high molecular weights, often in the region of ten times or more that of the typical primary coagulant (Letterman and Pero, 1990).

Information regarding the structure of polyelectrolytes can also be used to predict their toxicity effect. Biodegradation tends to decrease as the molecular weight increases and amorphous polymers generally biodegrade more rapidly than their crystalline counterparts. As halogenation of a polymer increases, biodegradation also tends to decrease (Hamilton et al, 1994). Polyelectrolytes often contain contaminants

derived from the manufacturing process, which can pose a health threat. These include (Letterman and Pero, 1990):

- residual monomers, for example acrylamide, ethylenimine and diallyldimethylammonium chloride,
- unreacted chemicals used in the production of the monomers such as epichlorhydrin, dimethylamine and formaldehyde,
- degradation products of residual monomer.
- inorganic salts, organic solvents and by-products of the organic catalysts used in the polymerisation reaction.

Furthermore, polyelectrolytes may also react with disinfectants such as chlorine to produce harmful by-products.

Processes have been introduced which limit these contaminants and careful monitoring and process control are required if the concentration of contaminants is to be kept low.

2.4. LEGISLATION

Concern regarding the health implications of polyelectrolytes prompted the AWWA to ask the US Public Health Service (USPHS) in 1957 about the safety of using these products for water treatment applications. In response the USPHS developed a programme to review polyelectrolyte safety and administered this until 1970 when the responsibility fell on the USEPA. As a result of this programme, a list of accepted products was drawn up and many American States used these for regulatory and advisory purposes. The list included a maximum dosage for each accepted product, but the USEPA stated that it did not approve, or in any way control the use of polyelectrolytes, serving only to offer advice in this regard (Letterman and Pero, 1990).

The USEPA decided on polyelectrolyte safety using technical information provided by the manufacturers. A copy of guidelines used by the USEPA was available, but the criteria used in determining whether a product could be listed as approved, were not mentioned (Letterman and Pero, 1990). By the end of December 1985 some 1 300 products produced by 134 manufacturers were listed by the USEPA. However, it is difficult to determine what polymers the different listed products contain, since the

USEPA assured manufacturers of confidentiality, but there are certainly a lot less compounds than there are products on the list. In fact, the literature (Hanson et al, 1993; Mangravirte, 1983; Halverson and Panzer, 1980) indicates that there are probably only 11 or 12 polymers associated with this list.

Limited resources and other demands restricted the USEPA's activities in managing this product approval list and in 1984, in an attempt to both deregulate the use of water treatment additives and shift the cost of product approval to the private sector, the USEPA proposed that a voluntary and objective body be established to continue with the programme (Letterman and Pero, 1990; McClelland et al, 1989). A consortium led by the National Sanitation Foundation (NSF) and consisting of the AWWA Research Foundation (AWWARF), the Conference of State Health and Environmental Managers (COSHEM) and the Association of State Drinking Water Administrators (ASDWA) was established and a few years later in 1987 the AWWA joined this group (McClelland et al, 1989).

NSF standards 60 and 61 were then introduced to protect public health by careful consideration of both the additive product and the contaminants which the product contributes to the water and they are based on the principle that the higher the exposure and the risk of a product or impurity, the more data that is required before granting approval for that substance. The maximum allowable limit (MAL) described in NSF standards 60 and 61 for regulated contaminants is based on the USEPA regulated maximum contaminant level (MCL), with the MAL being equal to 10% of the MCL. Contaminants are classified by four different concentration levels and toxicity testing determines in which level a contaminant is placed. McClelland et al, 1989, provide a detailed description of the procedure used in this classification.

There are presently more than 150 NSF-listed manufacturers in more than 25 countries worldwide and the NSF encourages enquiries from any organisation with an interest in potable water additives standards or the NSF's Listing Programme.

In Europe, EUREAU, which governs the European potable water sector, is largely influenced by the WHO guidelines. The first volume of the newly revised WHO guidelines were published in 1993 and it is clearly stated that the primary aim of these guidelines is the protection of public health. They also state that the guidelines are intended to provide a basis for the development of national standards that, if properly

implemented, will ensure the safety of drinking water supplies through the elimination or reduction to a minimum concentration of constituents of water known to be hazardous to health (Short Report, 1994).

A member state of the European Union is not obliged to adopt the new WHO guidelines into its legislation until such time as these are incorporated into the revised E.U. drinking water directive. The WHO guidelines are based on the precautionary principle and therefore if national standards vary from the WHO guidelines it does not necessarily mean that the health protection is being compromised. The WHO guidelines state that the amount by which and the period for which any guideline value can be exceeded without affecting public health depends upon the substance in question (Short Report, 1994).

As far as polyelectrolytes are concerned, the WHO guidelines refer only to epichlorhydrin and acrylamide and state that since these compounds can hardly be detected in water using the normal routine measurements, their presence in water needs to be limited through legislation and normalisation for chemicals and materials which come into contact with drinking water. Certain European countries, like France appear to have taken the initiative in this regard and have established their own legislation regarding the use of polyelectrolytes in drinking water treatment.

The situation in South Africa prior to 1994 was that the Department of Health issued certification for water treatment chemicals on an ad hoc basis, subject to the supplier being able to supply approval or certification for his product or the monomer/s from a recognised world health body such as the World Health Organisation (WHO), the USEPA and the European Economic Community (EEC). After 1994 the issuing of such certification by the Department of Health fell away altogether. The Department of Health is currently working on a new national system for the purpose of regulating these chemicals.

2.5. EVALUATION OF COAGULANTS

Essentially coagulants are evaluated for two reasons, firstly to choose the best coagulant in terms of performance and cost and secondly to ensure consistent quality of the product. When choosing a suitable primary coagulant (i.e. a coagulant for removal of particulates and/or humic and other organic compounds from a water), the

jar test remains the most effective tool for this application (see Section 2.6.1). The jar test is of course a batch process and not continuous as is generally the case at full-scale plant operation, but it is a very versatile test that can be used for the following (Water Quality and Treatment, 1990):

1. Coagulant selection
2. Dosage selection
3. Coagulant aid type and dosage selection
4. Determination of optimum pH (only a factor with inorganic coagulants which are pH sensitive)
5. Determination of best settlement and /or filtration methods.

It is also important to select products which have approval from the NSF, WHO or another reputable organisation, since the safety of the water can then be guaranteed.

It is always preferable to carry out tests on a number of samples and if possible, under different conditions to establish the most reliable product. Having selected a suitable product, the use of routine jar tests remains necessary for a number of reasons:

- the nature and quality of the raw water may change, which may affect the coagulant dose.
- it is necessary to check that the plant dosage matches the demand established in the laboratory.
- different batches of coagulant may vary and the use of comparative jar tests using some of the original product sample is a useful quality check. This is particularly the case with polyelectrolytes, but inorganic coagulants such as aluminium sulphate and ferric salt solutions sometimes also vary in strength and can also be assessed using a jar test.

2.5.1. RECOMMENDED PROCEDURE FOR COAGULANT SELECTION

When choosing a new coagulant for a water treatment works, various manufacturers should be invited to submit samples for evaluation. Each manufacturer should be limited to a small number of samples, possibly 2 or 3, otherwise assessment can become laborious and very time consuming due to the large number of samples. Jar tests should be conducted as described in Section (2.6.1) on raw water collected at the inlet to the works and using the coagulants to be assessed. It is advisable to simulate the plant conditions as closely as possible, adding other chemicals such as

chlorine and lime, if these are being used, in concentrations similar to those being used on the plant. The jar test can also be used to determine the optimal addition point of chemicals, for example, whether it is better to add the lime prior to the coagulant, or after the coagulant.

The jar tests should preferably be conducted on a single water sample (i.e. collected from the same sampling point at the same time) as this provides a better comparison of the different coagulants. Also, if possible, a number of jar tests should be conducted over a period of time, which will allow a better assessment of the seasonal variations of the water and the impact that these have on the performance of the various coagulants.

Once the jar tests have been completed, the data should be collated and the best coagulants in terms of both performance and cost should be determined. The best products (usually 2 to 4) should then be selected for plant trial evaluation. It is highly recommended that plant trials be conducted whenever possible, since the jar test is not infallible and a true assessment of the coagulant is only possible at plant scale. Plant trials should be conducted for a minimum of three weeks and preferably six weeks for each coagulant in order to obtain a true reflection of the performance of each chemical. Periods shorter than this may not be long enough to allow complete eradication of the previously used coagulant from the floc blanket. During plant trials confirmatory jar tests can also prove invaluable. This was made evident in a recent case study at Umgeni Water. During trials at the Umlaas Road WW, a change in water quality occurred, by coincidence, at almost the same time that the change-over from one coagulant to another took place. This change was not evident from routine water quality parameters, but jar tests revealed an increase in the optimum dose of all four coagulants being assessed. Had the jar tests not been conducted, it would have appeared as though the third coagulant used on the plant trial was far less effective than the previous two coagulants. The jar tests revealed that this was not in fact the case.

2.5.2. ENSURING CONSISTENT COAGULANT QUALITY

Once a coagulant has been selected, it is important to ensure that the quality of the chemical remains constant between deliveries. Jar tests can be used for this purpose, but simpler, more rapid tests can be used to determine whether certain important parameters are remaining consistent between deliveries. In the case of inorganic

coagulants such as aluminium sulphate or ferric chloride, the measurement of SG, which is both rapid and simple using a hydrometer, can be carried out. In the case of polymeric coagulants, parameters such as the pH, viscosity, density and total solids can be affected by changes in the manufacturing process and can be easily determined (see Sections 2.7.1; 2.7.2; 2.7.3; and 2.7.4). Only if one of these parameters differs by more than an acceptable amount from the average value (± 10%), are jar tests required in order to determine whether the performance of the questionable batch differs from that of a sample of the original tender sample. Many of the polymeric coagulants also contain polyaluminium chloride, so determination of the aluminium content of the coagulant can also be used for quality control.

In the case of inorganic coagulants such as aluminium sulphate and ferric salts, quality control of deliveries can be carried out by analysing parameters such as specific gravity, acidity, insoluble matter and active ion (e.g. aluminium, iron) (see Sections 2.8.1; 2.8.2; 2.8.3; 2.8.4; 2.8.5; 2.8.6; 2.8.7; 2.8.9; 2.8.10). Other common tests like ferrous ion content of ferric salts and moisture content of granular forms of the coagulants can be used to determine purity and quality as well as being used as quality control measures (see Sections 2.8.8; 2.8.11; 2.8.12; 2.8.13).

Another test that can be used on-site to monitor plant performance is known as the Cascade test. This is similar to the jar test, except that the dosing of treatment chemicals takes place on the plant. Samples are then collected of the dosed water prior to entering the clarifiers and flocculation and settling are simulated using the jar test apparatus. This tests allows the plant operator a rapid means of assessing the impact of various changes in treatment chemical type and dose on plant performance without waiting for the full effects of a dosage change to pass through the works (see Section 2.6.2).

2.6. ANALYTICAL METHODS: DOSAGE TESTS

2.6.1. STANDARD JAR TEST

1. Introduction

Jar tests are used to predict clarification at water works. There are four main factors that can influence clarification performance, namely the raw water quality, mixing conditions, coagulant chemistry and dosage rate.

2. Scope

This method may be used to determine optimum dose of an inorganic coagulant or a polyelectrolyte for use as a primary coagulant and for comparing the performance of different coagulants.

3. Interferences

Interferences are caused by changes in raw water conditions, such as temperature, pH, chlorine, plant design and mixing energies.

4. Hazards

Ensure that you are familiar with the dangers and treatment associated with these coagulants.

5. Sample Collection

Samples may be collected in 25 L drums or any other suitable containers.

6. Apparatus

1. Pipettes
2. Jar Stirrer, preferably 6 paddle
3. Tall-form square or round 1 L beakers
4. Standard volumetric glassware
5. pH meter
6. Funnels
7. 500 mL conical flasks
8. 24 cm MN 614 filter paper, Whatman No.1 filter paper or equivalent.

7. Reagents

1. Coagulants or Polymers to be assessed. All solutions are made up in tap or distilled water. Weights and volumes given below are intended only as a guideline. Different laboratories may choose to use solutions of different strength with different volumes of water sample.
2. Polyelectrolyte coagulant solution
    - Weigh out 0,8 g of polyelectrolyte solution into a beaker
    - Transfer to a 1 L volumetric flask and dilute to mark.
    - May be stored for 1 week.
    - 1 mL polyelectrolyte solution will be equal to 1 mg/L dosage (in 800 mL)
3. Inorganic Coagulant Solution
    - Weigh out 0,8 g (1 mL = 1 mg/L) or 4,0 g (1 mL = 5 mg/L) or 8,0 g (1 mL = 10 mg/L) of aluminium sulphate or ferric chloride (ensure that the weight used takes into account the concentration of the coagulant solution as supplied. e.g. to obtain a 4,0g/L as active alum when using a 48% alum solution, 8,33 g/L of 48% alum solution will be required. If the SG has been measured, then a measured volume can be used instead of a mass).
    - Transfer to a 1 L volumetric flask and dilute to the mark
4. Lime solution
    - Weigh out 0,8 g (1 mL = 1 mg/L) or 4 g (1 mL = 5 mg/L) of white or brown lime depending what is used on the works.
    - Transfer to a 1 L volumetric flask and dilute to mark
    - May be stored for 1 week.

8. Analytical Procedure

1. Obtain a raw water sample from the raw water inlet before addition of any chemicals and excluding filter washwater return.
2. Determine the turbidity, pH, temperature and any other relevant treatment measurement on the raw water sample and record results on report sheet.
3. Measure out 800 mL aliquots of raw water into the number of beakers on the jar test machine and number them accordingly. The volumes provided here are intended only as a guideline. Different laboratories may choose to use solutions of different strength with different volumes of water sample..

3. Set the flashmix speed at a speed which best simulates the conditions on the plant (this is generally between 100 and 300 rpm) and start the stirrer.
4. Add coagulant solution to all the beakers simultaneously or within as short a time as possible, in a range of doses based on previous experience. Coagulant can be added using a specially designed manifold apparatus in which the coagulant dose for each jar can be added to a small beaker or test tube and then the manifold tipped so that the coagulant dose for each jar is added simultaneously. Alternatively, one can use a separate syringe or beaker for the coagulant dose for each jar. If the syringes or beakers are filled first, it is possible to add the coagulant to each of the jars within a very short period of time.
5. If the water is unfamiliar, commence with a dosage range of 1 to 6 mg/L for polyelectrolyte, or 5 to 30 mg/L for ferric chloride, or 10 to 60 mg/L for alum, and adjust for further jar tests if necessary for less turbid waters. Higher doses may be required for more turbid waters.
6. If using alum or ferric chloride add lime at a dosage of $^1/_4$ or $^1/_3$ the coagulant dosage respectively
7. Stir for 2 minutes
8. After 2 minutes reduce the speed to 40 rpm for a further 15 minutes.
9. Turn off the stirrer and record the floc size, based on the standard floc sizes shown on the 'Floc comparator' at the bottom of the jar test worksheet.
10. Record the settling rate, i.e. slow, moderate or rapid settling.
11. If required, allow the water to settle for specific period of time and then carefully withdraw sufficient water from just below the surface using a pipette, syringe or similar and measure the turbidity or whichever parameter is used for meeting the treatment objectives.
12. Filter each sample through 24 cm MN615 filter papers or Whatman No. 1 filter papers or equivalent into 1 L conical flasks.
13. Collect about 200 mL of filtrate in the flask and rinse. Discard the washings.
14. Filter the remaining sample.
15. Measure the filtered sample for pH, turbidity or any other parameter important in terms of the treatment objectives.
16. Record the results on report sheets.
17. The turbidity should be less than the specified maximum (generally 0,5 NTU or 1 NTU). If colour, total organic carbon or any other parameter is important in meeting the treatment objectives, measure these too and choose the lowest

coagulant dose which reduces the relevant parameter to below the specified maximum value.

18. If the turbidity (or any other treatment parameter) is greater than the specified maximum, repeat the exercise starting at a higher or lower dose as relevant, until the optimum dose is achieved.

9. Calculation

Based on treatment requirements, performance and cost, the optimum dose and most suitable coagulant can be determined.

10. References

1. Process Services, Umgeni Water.

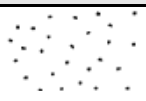
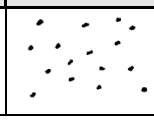
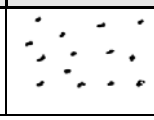
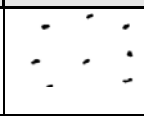
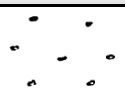
STANDARD JAR TEST EVALUATION

Sample	
Date Taken	
Location	
Sample size	
Date sample analysed	

RAW WATER DETAILS

pH		**Colour**			
Turbidity					
Temp					

Chemicals						
	1	**2**	**3**	**4**	**5**	**6**
Alum mg/L						
Polymer mg/L						
Lime mg/L						
Pre Cl_2 mg/L						
Post Cl_2 mg/L						
Bentonite mg/L						
Flash Mix						
Flash Mix Time						
Slow Mix Speed						
Slow Mix Time						
pH						
Turbidity, NTU						
Temperature °C						
Colour ° Hazen						
Floc size						
Settling rate						

A	B	C	D	E	F
					

2.6.2. CASCADE TEST

1. Introduction

The cascade test is a modification of the jar test, in which the water used has already been chemically dosed on the plant. This test allows plant operators to rapidly evaluate the effect of chemical dosing on final water quality.

2. Scope

This method may be used to confirm the present plant conditions and give the operational staff time to make adjustments if necessary.

3. Interferences

Interferences are caused by change in raw water conditions, i.e. temperature, pH, chlorine, plant design, or mixing energies.

4. Sample Collection

Samples may be collected in suitable containers.

5. Apparatus

1. Pipettes
2. Jar stirrer, preferably 6 paddle
3. Tall-form square or round 1 L beakers
4. Standard volumetric glassware
5. pH meter
6. Funnels
7. 500 mL conical flasks
8. 24 cm MN615 filter paper, Whatman no1 filter paper or equivalent.

6. Reagents

Coagulants and other treatment chemicals being used on the plant at the time of sample collection, such as lime, powdered activated carbon, chlorine etc. will already be present in the water sample.

7. Analytical Procedure

1. Obtain a dosed raw water sample at pre-selected points on the plant, immediately before it enters the clarifiers/ sedimentation basins.
2. Determine the turbidity, pH, temperature and any other relevant treatment measurement on the raw water sample and record results on report sheet.
3. Measure out 800 mL aliquots of raw water into a beaker (this volume is intended as a guideline only and can be adjusted to suit the needs of the analyst).
4. Set the slow mix speed as required (generally around 40 rpm) for 15 minutes.
5. Turn off the stirrer and record the floc size, based on the standard floc sizes shown on the 'Floc comparator' at the bottom of the jar test worksheet
6. Record the settling rate, i.e. slow, moderate or rapid settling
7. Filter each sample through 24 cm MN615 filter papers or Whatman No. 1 filter papers or equivalent into 1 L conical flasks.
8. Collect about 200 mL of filtrate in the flask and rinse. Discard the washings.
9. Filter the remaining sample.
19. Measure the filtered sample for pH, turbidity or any other parameter important in terms of the treatment objectives.
10. Record the results on report sheets.
11. The turbidity should be less than the specified maximum (generally 0,5 NTU or 1 NTU). If colour, total organic carbon or any other parameter is important in meeting the treatment objectives, measure these too.
12. If the turbidity (or any other treatment parameter) is greater than the specified maximum, repeat the exercise starting at a higher or lower dose as relevant, until the optimum dose is achieved. Choose the lowest coagulant dose which reduces the relevant parameter to below the specified maximum value.

8. References

1. Process Services, Umgeni Water.

2.7. ANALYTICAL METHODS: POLYELECTROLYTE TESTS

2.7.1. pH OF A POLYMERIC COAGULANT SOLUTION

1. Introduction

To see if a solution is acidic, neutral, or basic depends on the hydronium–ion (hydrogen-ion) concentration. The acidity can be quantitatively described by giving the hydronium-ion concentration. These concentrations are very small and it is often more convenient to give the acidity using pH, which is defined as the negative of the logarithm of the molar hydronium–ion concentration.

2. Scope

This method may be used to determine the pH of a polymeric coagulant.

3. Interferences

Temperature changes, expired buffered solutions, or poorly maintained electrodes may cause interferences.

4. Hazards

5. Sample Collection

Samples may be collected in plastic or glass bottles.

6. Apparatus

1. pH meter
2. pH electrode
3. Thermometer or a temperature compensation probe
4. Glass beakers

7. Reagents

pH reference buffer solutions above and below the pH range to be measured.

8. Analytical Procedure

1. Standardise the pH meter with the buffer solutions above and below the pH range to be tested.
2. Add the polymer solution to the beaker.
3. If no temperature compensation probe is available, record the temperature reading.
4. Measure the pH of the polymer solution.
5. Thoroughly rinse the electrodes after each test.

9. Calculation

Read pH value on meter.

10. References

1 Umgeni Water South African National Accreditation Services method.

2.7.2. MEASURING THE DENSITY OF POLYMERIC COAGULANTS

1. Introduction

The density of an object is described as its mass per unit volume. We express this as D = M/V. Density is characteristic of a substance and can therefore be helpful in identifying it. Density is also useful in determining whether a substance is pure.

2. Scope

This method may be used to measure the density of a polymeric coagulant.

3. Interferences

Temperature

4. Hazards

None

5. Sample Collection

Samples may be collected in glass or plastic containers.

6. Apparatus

1. Analytical balance
2. Volumetric flasks 50 mL
3. Dropper pipettes

7. Reagents

None

8. Analytical Procedure

1. Place the volumetric flask on the balance and tare (zero).
2. Remove the flask from the balance and place on a clean dry surface.
3. Place a tiny funnel into the flask and carefully add the polymer to the flask with a dropper without obtaining any polymer on the sides of the flask.
4. Fill the flask to the 50 mL mark and return to the balance.
5. Record the weight.

9. Calculations

$$\text{Density} = \frac{\text{mass of polymer in flask}}{\text{volume of flask}}$$

10. References

1. "Standard Methods for the Examination of Water and Wastewater", 20th Edition, Edited by Clesceri, L S; Greenberg, A E; and Eaton, A D, Pub. AWWA, 1998
2. Umgeni Water South African National Accreditation Services method.

2.7.3. VISCOSITY FOR POLYMERIC CATIONIC COAGULANTS

1. Introduction

Viscosity is the ability of a liquid to resist various internal and external movements, such as flow. In the case of polymeric coagulants, the viscosity is affected by a number of factors, such as the degree of polymerisation and the concentration of the active ingredient. Viscosity can therefore be a good quality control indicator, indicating consistency in the product and whether changes, which may affect the activity of the coagulant, might have occurred.

2. Scope

This method may be used to determine the viscosity of a polymeric cationic coagulant.

3. Interferences

Temperature. Polymeric cationic coagulants are thixotropic, such that their viscosity will decrease with increasing spindle speed.

4. Hazards

None

5. Sample Collection

Samples may be collected in either glass or plastic containers.

6. Apparatus

1. Viscometer, Brookfield, Model LVT or equivalent.
2. Tall form 250 mL beaker

7. Reagents

Distilled water

8. Analytical Procedure

1. Set up the viscometer and level the instrument. These instructions are for a Brookfield Model LVT. For other viscometers, follow the manufacturer's instructions.
2. Attach the spindle specified by the polymer supplier. (NOTE: Left-handed threads.)
3. Pour enough sample into the beaker to cover the spindle up to the groove.
4. Lower the viscometer with the spindle attached into the sample until the surface of the sample meets the groove on the spindle shaft. The spindle should not touch the bottom of the beaker.
5. Set the viscometer to chosen revolutions per minute.
6. Turn on the viscometer motor.
7. After the needle reaches a steady reading, and after at least 10 revolutions, depress the clutch lever on the back of the viscometer to "freeze" the needle on the scale.
8. With the clutch depressed, stop the viscometer motor when the needle is visible in the viscometer window.
9. Read and record the position of the needle on the scale.
10. Repeat the procedure until you have three readings.
11. If the manufacturer does not specify a spindle, start with spindle number 1 and follow the procedure. If the needle is not near the middle of the of the viscometer's scale range, use the next spindle size up and repeat until a correct reading has been obtained.

9. Calculation

Average the three readings.

Obtain the Brookfield viscosity by multiplying the average reading calculated by the factor for that spindle and speed supplied by the viscometer manufacturer.

10. References

1 ANSI/AWWA B451-98

2.7.4. TOTAL SOLIDS OF A POLYMERIC COAGULANT SOLUTION

1. Introduction

This procedure is one of several that are applicable to determining the total solids content of a polymeric coagulant. Note that this procedure is not corrected for inert ingredients and therefore, it may not give the polymer content of the sample.

2. Scope

This method may be used to confirm the total solids of a polymeric coagulant.

3. Interferences

Incorrect oven temperatures.

4. Hazards

None

5. Sample Collection

Samples may be collected in glass or plastic containers.

6. Apparatus

1. Analytical balance
2. Aluminium weighing dish
3. Forced draft oven
4. Desiccator and desiccant

7. Reagents

None

8. Analytical Procedure

1. Heat aluminium weighing dishes in oven at 105º C to110º C for a minimum of 1 hour, remove and cool in the desiccator.
2. Record the tare weight of dried aluminium dish to the nearest 0,0001 g (M1).
3. Remove the weighing dish from the balance and add approximately 30 to 40 g of polymer to the dish; return to the balance.

4. Record the total weight of the dish and polymer to the nearest 0,0001 g (M2).
5. Place the aluminium weighing dish containing the weighed sample in a 105º C to 110º C forced draft oven for a minimum of 3 hours.
6. Remove the aluminium dish from the oven and cool in the desiccator. Weigh the cooled dish to the nearest 0,0001 g (M3).

9. Calculations

$$\% \text{ Total solids} = \frac{M3 - M1}{M2 - M1} \times 100$$

Where:

M1 = Mass of empty dish

M2 = Mass of dish and sample before drying (initial sample)

M3 = Mass of dish and dry sample

Notes: Samples should be run in duplicate.

The difference between the duplicate samples should be less the ± 0,5%.

10. References

1. "Standard Methods for the Examination of Water and Wastewater", 20th Edition, Edited by Clesceri, L S; Greenberg, A E; and Eaton, A D, Pub. AWWA, 1998
2 Umgeni Water South African National Accreditation Services method.

POLYMERIC COAGULANT QUALITY CONTROL

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

VISCOSITY	**pH**

SPECIFIC GRAVITY			
Sample 1	**Sample 2**	**Sample 3**	**Density**

TOTAL SOLIDS		
Mass 1	**Mass 2**	**Mass 3**

$$\% \text{ TOTAL SOLIDS} = \frac{M3 - M1}{M2 - M1} \times 100$$

Where:

M1 = Mass of empty dish

M2 = Mass of dish and sample before drying (initial sample)

M3 = Mass of dish and dry sample

2.8. ANALYTICAL METHODS: INORGANIC COAGULANTS

2.8.1. DENSITY OF COMMERCIAL ALUMINIUM SULPHATE SOLUTION

1. Introduction

The density of an object is described as its mass per unit volume and is expressed as:

$$D = M/V.$$

Since density is characteristic of a substance, it can be helpful in identifying it, as well as being useful in determining the concentration of the substance in solution form.

2. Scope

This method may be used to measure the density of aluminium sulphate solution, thereby allowing determination of the percentage of aluminium sulphate present in the solution.

3. Interferences

Temperature

4. Hazards

Corrosive, wear gloves when handling.

5. Sample Collection

Samples may be collected in plastic containers.

6. Apparatus

1. Analytical balance
2. Volumetric flasks 50 mL
3. Dropper pipettes

7. Reagents

None

8. Analytical Procedure

1. Place the volumetric flask on the balance and tare (zero).
2. Remove the flask from the balance and place on a clean dry surface.
3. Place a tiny funnel into the flask and carefully add the alum to the flask with a dropper without obtaining any alum on the sides.
4. Fill the flask to the 50 mL meniscus and return to the balance.
5. Record the weight.

9. Calculations

$$\text{Density} = \frac{X}{50} \text{ (g/mL)}$$

Where: X = mass in grams

In the case of a solution, the density (in g/mL) is numerically equal to the specific gravity (SG).

Refer to **Table 2.1** below for the conversion of SG to % aluminium sulphate.

10. References

1. Umgeni Water South African National Accreditation Services method.

TABLE 2.1: S.G. of Commercial Aluminium Sulphate Solutions at 15ºC

Specific Gravity	% Alum Sulphate	Specific Gravity	% Alum Sulphate
1,01	1,88	1,19	30,2
1,02	3,68	1,20	31,6
1,03	5,44	1,21	32,9
1,04	7,18	1,22	34,2
1,05	8,94	1,23	35,6
1,06	10,6	1,24	37,0
1,07	12,3	1,25	38,4
1,08	13,9	1,26	39,7
1,09	15,4	1,27	41,0
1,10	17,0	1,28	42,3
1,11	18,5	1,29	43,7
1,12	20,1	1,30	45,0
1,13	21,5	1,31	46,2
1,14	23,0	1,32	47,5
1,15	24,4	1,33	48,8
1,16	25,9	1,34	50,1
1,17	27,4	1,35	51,3
1,18	28,8		

2.8.2. BASICITY OR FREE ACID OF COMMERCIAL ALUMINIUM SULPHATE SOLUTION

1. Introduction

As early as the 17th century various forms of aluminium sulphate have been used for the coagulation of suspended and colloidal particles in water. Aluminium sulphate used to be added to the water in lump or slab form and is prepared from aluminium hydroxide, alumina trihydrate, or alumina-bearing ores, such as clay and bauxite. The aluminium ore is ground to the required fineness and digested with sulphuric acid at elevated temperatures. The basicity or acidity of a solution influences corrosion, chemical reaction rates, chemical speciation and biological processes (Standard Methods, 1998).

2. Scope

This method maybe used to confirm the basicity or free acid of liquid aluminium sulphate. This method is based on the decomposition of aluminium salts by an excess of neutral potassium fluoride to form two stable compounds neutral to phenolphthalein, whereas any free acid remains unaltered.

3. Interferences

Temperature

4. Hazards

Corrosive, wear gloves when handling.

5. Sample Collection

Samples may be collected in plastic containers.

6. Apparatus

1. Analytical balance
2. 2 L volumetric flask
3. Beakers
4. Weighing boats
5. Erlenmeyer flasks

7. Reagents

1. Phenolphthalein indicator
2. Potassium Fluoride solution
    - Dissolve 1,000 g of pure potassium fluoride in 1 200 mL of hot, carbon dioxide free distilled water and 0,5 mL of phenolphthalein solution.
    - Neutralise with potassium hydroxide or sulphuric acid. To confirm that the neutralisation is correct, add 1 mL of solution to 10 mL of distilled water, a faint pink colour should be observed.
    - Upon neutralisation, filter out the insoluble matter without washing and dilute to 2 L, with carbon dioxide free water. Store in a plastic bottle.
3. 0,5 N Sulphuric acid solution
    - Filter about 500 mL of distilled water into a 1 L volumetric flask. Add 14 mL of concentration sulphuric acid and dilute to 1 L with distilled water.
4. 0,5 N Sodium Hydroxide solution
    - Weigh out 20 g of sodium hydroxide pellets in to a beaker, dissolve in distilled water and pour into a 1 L volumetric flask and dilute to 1 L. Standardise the sodium hydroxide against the sulphuric acid in 40 mL of distilled water to which 10 mL of potassium fluoride solution has been added, use phenolphthalein as the indicator. Standardise against benzoic acid or potassium acid pthalate before using.

8. Analytical Procedure

1. Weigh out 7 g of liquid alum into an Erlenmeyer flask. Record the exact weight.
2. Add 100 mL of distilled water to the flask and heat to boiling.
3. Add 10 mL of 0,5 N sulphuric acid to the hot solution.
4. Cool to room temperature
5. Add 18 to 20 mL of potassium fluoride solution and 0,5 mL of phenolphthalein indicator.
6. Titrate against 0,5 N sodium hydroxide, dropwise, until a slight pink colour persists for 1 minute.
7. The titration is an indication of whether the sample is acidic or basic.

9. Calculations

$$\% \text{ Free alumina } (Al_2O_3) = \frac{(\text{mL } 0{,}5N\ H_2SO_4 - \text{mL } 0{,}5N\ NaOH) \times 0{,}0085 \times 100}{\text{weight of sample}}$$

$$\% \text{ Free sulphuric acid } (H_2SO_4) = \frac{(\text{mL } 0{,}5NaOH - \text{mL } 0{,}5N\ H_2SO_4) \times 0{,}0245 \times 100}{\text{weight of sample}}$$

Basic alumina exists if the sodium hydroxide back titration is less than the amount of sulphuric acid added (i.e. less than 10 mL). Free acid exists if the sodium hydroxide back titration is more than the amount of sulphuric acid added (i.e. is greater than 10 mL). The sample is neutral if the sodium hydroxide back titration is equal to the sulphuric acid added.

10. References

1. ANSI/AWWA B403-98

2.8.3. WATER-INSOLUBLE MATTER OF DRY AND LIQUID ALUM

1. Introduction

Water-insoluble matter in liquid alum should be kept to a minimum, since is does not take part in the coagulation reaction, adds to sludge formation and may introduce undesirable particulates into the water.

2. Scope

This method may be used to confirm the water insoluble matter of liquid aluminium sulphate.

3. Interferences

Temperature

4. Hazards

Corrosive, wear gloves when handling.

5. Sample Collection

Samples may be collected in plastic containers.

6. Apparatus

1. Analytical balance
2. Gooch crucibles
3. Filter papers
4. Tongs

7. Reagents

None

8. Analytical Procedure

1. Into a Gooch crucible place a glass-fibre filter paper, dry at 105º C to 110º C for at least an hour.
2. Cool in desiccator and record weight when cool.

3. Weigh out 40 g of liquid alum or 20 g of dry alum sulphate and dilute to 150 mL with hot distilled water and stir.
4. Filter through the prepared crucible. Rinse the residue with hot distilled water until the filtrate is free of sulphates. This should be at least 3 washings of 25 mL each.
5. Return the crucible to the oven and for at least 1 hour or to a constant weight.
6. Cool in desiccator and weigh, record weight.

9. Calculations

$$\% \text{ Insoluble matter} = \frac{\text{weight of insoluble residue} \times 100}{\text{weight of sample}}$$

10. References

1. ANSI/AWWA B403-98

ALUMINIUM SULPHATE QUALITY CONTROL

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

SPECIFIC GRAVITY/ DENSITY			
Sample 1	**Sample 2**	**Sample 3**	**Density**

BASICITY OR FREE ACID	
Mass of liquid alum g	
Blank	
Titre 1	
Titre 2	
Titre 3	

WATER – INSOLUBLE MATTER	
Mass of gooch crucible + filter paper	
Weight of liquid or dry alum g	
Mass of gooch crucible + sample	
% Insoluble matter	

2.8.4. DENSITY OF COMMERCIAL FERRIC CHLORIDE SOLUTION

1. Introduction

The density of an object is described as its mass per unit volume. We express this as:

$$D = M/V$$

Density is characteristic of a substance, it can be helpful in identifying it. Density is also useful in determining whether a substance is pure and in measuring the concentration of the solution.

2. Scope

This method maybe used to confirm the density of a ferric chloride solution thereby identifying the percentage of ferric chloride.

3. Interferences

Temperature

4. Hazards

Corrosive, wear gloves when handling.

5. Sample Collection

Samples may be collected in plastic containers.

6. Apparatus

1. Analytical balance
2. Volumetric flasks 50 mL
3. Dropper pipettes

7. Reagents

None

8. Analytical Procedure

1. Place the volumetric flask on the balance and tare (zero).
2. Remove the flask from the balance and place on a clean dry surface.
3. Place a tiny funnel into the flask and carefully add the ferric to the flask with a dropper without obtaining any ferric on the sides.
4. Fill the flask to the 50 mL meniscus and return to the balance.
5. Record the weight.

9. Calculations

$$\text{Density} = \frac{\text{(reading on the balance)}}{50} \text{ (g/mL)}$$

For a solution, the density (in g/mL) is numerically equal to the specific gravity (SG). Refer to **Table 2.2** below for the conversion of SG to % ferric chloride.

10. References

1. ANSI/AWWA B407-93
2. Umgeni Water South African National Accreditation Services method.

TABLE 2.2: S.G. of Commercial Ferric Chloride Solution

Specific Gravity	% Ferric Chloride
1,0025	0,50
1,0068	1,00
1,0153	2,00
1,0238	3,00
1,0323	4,00
1,0408	5,00
1,0493	6,00
1,0580	7,00
1,0668	8,00
1,0760	9.00
1,0853	10,00
1,1040	12,00
1,1228	14,00
1,1420	16,00
1,1615	18,00
1,1816	20,00
1,2234	24,00
1,2679	28,00
1,3153	32,00
1,3654	36,00
1,4176	40,00

2.8.5. ACIDITY OF FERRIC CHLORIDE

1. Introduction

It is important to know the acidity of a solution, since acidity is a factor in corrosivity, it influences the rate of chemical reactions and affects chemical speciation and biological processes. This method is for the determination of acidity in ferric chloride in the liquid form.

2. Scope

This method maybe used to confirm the acidity of liquid ferric chloride.

3. Interferences

4. Hazards

Contact with skin may cause irritation, wear gloves. Wear goggles as ferric chloride solution may cause burns to the eyes.

5. Sample Collection

Samples may be collected in plastic or glass containers.

6. Apparatus

1. Analytical balance
2. 1 L volumetric flasks
3. 50 mL beakers
4. 50 mL bulb pipettes
5. Erlenmeyer flasks

7. Reagents

1. Potassium fluoride ($KF.2H_2O$) reagent grade
2. Phenolphthalein indicator
3. Sodium hydroxide (1 N and 0,05 N)
    - For a 1 N NaOH solution, weigh out 40 g of sodium hydroxide pellets and dissolve in 200 mL of CO_2-free distilled water. Make up to 1 L in a volumetric

flask. Standardise against benzoic acid or potassium acid phthalate of known normality before using.

- For a 0,05 N solution, dilute 50 mL of 1 N sodium hydroxide to 1 L with CO_2-free distilled water.

4. Sulphuric Acid
   - For 0,05 N sulphuric acid dilute 50 mL of concentrated sulphuric acid (36 N) to 1 L. This will give you an 1,8 N solution take 28 mL of this 1,8 N solution and dilute to 1 L thereby producing a 0,05 N solution.
   - Standardise the acid using a known base before using.

8. Analytical Procedure

1 Weigh out 20 g of potassium fluoride
2 Dissolve the potassium fluoride in 40 mL of boiling water.
3 Add 0,2 mL of phenolphthalein indicator solution.
4 Add 0,05 N sodium hydroxide dropwise until a faint pink colour persists.
5 The above solution is the neutralised potassium fluoride.
6 Weigh 1 to 2 g (1 mL) of ferric chloride and record mass.
7 Wash the ferric chloride into a 250 mL Erlenmeyer flask with 50 mL of boiled distilled water.
8 Add 25 mL of neutralised potassium fluoride and mix.
9 Add 0,2 mL of phenolphthalein indicator solution and titrate to a faint pink colour with 0,05 N sodium hydroxide.

9. Calculations

$$\% \text{ Free acidity (HCL)} = \frac{\text{mL 0,05 N NaOH x 0,001825 x 100}}{\text{g of sample}}$$

10. References

1. ANSI/AWWA B407-93.

2.8.6. TOTAL INSOLUBLE MATTER FOR FERRIC CHLORIDE

1. Introduction

Ferric chloride is commercially available in two solid forms, hexahydrate and anhydrous, or in liquid form. Ferric chloride is an orange- brown aqueous solution that is acidic and corrosive to common metals. This method is for ferric chloride in the liquid form.

2. Scope

This method maybe used to confirm the insoluble matter of liquid ferric chloride.

3. Interferences

4. Hazards

Contact with skin may cause irritation, wear gloves. Wear goggles as ferric chloride solution may cause burns to the eyes.

5. Sample Collection

Samples may be collected in plastic or glass containers.

6. Apparatus

1. Analytical balance
2. Membrane filter holder 47 mm or 110 mm
3. Glass fibre filters Whatman GF/C or equivalent
4. Filter flask

7. Reagents

The ferric chloride sample that is to be tested.

8. Analytical Procedure

1. Dry the filter paper in an oven at 103ºC for 30 minutes.
2. Cool in desiccator and weigh to the nearest mg. This is the tare weight.
3. Place the filter, wrinkled side up, in the filter holder.
4. Apply a vacuum and wet with a small amount of distilled water.

5. Tare a 250 mL beaker, shake sample and immediately pipette 25 mL into the beaker.
6. Record the weight of the sample. This weight will be used in the calculation for percent total insoluble matter.
7. Add approximately 150 mL of distilled water to the weighed ferric chloride and filter.
8. Wash the residue in the beaker onto the filter.
9. Wash the filter repeatedly with distilled water until the filtrate is no longer yellow in colour.
10. This will take at least six washings.
11. Remove the filter and dry in an oven at 103º C for at least and hour or until a constant weight, remove and cool in desiccator.
12. Weigh to the nearest mg.
13. Subtract the tare weight. This is the weight of the residue to be used in the calculation for percent total insoluble matter.

9. Calculations

$$\% \text{ Total insolubles} = \frac{\text{weight of residue} \times 100}{\text{weight of sample}}$$

10. References

1. ANSI/AWWA B407-93

2.8.7. TOTAL IRON CONTENT OF COMMERCIAL FERRIC CHLORIDE SOLUTION

1. Introduction

The total iron content of a ferric chloride solution is important, since iron is the active ingredient. This method will however measure all iron present, including ferric and ferrous ions, although it is the ferric ions which take part in coagulation reactions. A method for determining concentration of ferrous ion is described in Section 2.8.8. This method is for total iron determination of ferric chloride in the liquid form.

2. Scope

This method maybe used to confirm the iron content of liquid ferric chloride solution thereby identifying the percentage of iron.

3. Interferences

4. Hazards

Contact with skin may cause irritation, wear gloves. Wear goggles as ferric chloride solution may cause burns to the eyes.

5. Sample Collection

Samples may be collected in plastic or glass containers.

6. Apparatus

1. Analytical balance
2. Volumetric flasks 1 L
3. Measuring cylinders

7. Reagents

1. Concentrated sulphuric acid
2. Concentrated hydrochloric acid
3. Stannous chloride solution

- Dissolve 100 g of stannous chloride in 30 percent-by-volume hydrochloric acid solution (HCL/ H_2O). This solution is stable for approximately 1 month, discard if the solution becomes cloudy.

4. Saturated mercuric chloride solution
   - Into 500 mL of distilled water dissolve mercuric chloride until no additional mercuric chloride will dissolve.
5. Sulphuric acid/phosphoric acid solution
   - Into a 1 L volumetric flask add 500 mL of distilled water. To this water add 150 mL of sulphuric acid and 150 mL of phosphoric acid , make up to a litre.
   - **Remember to pour acids into water.**
6. Potassium dichromate solution
   - Dissolve 4,902 g of previously dried reagent grade potassium dichromate in distilled water. This is a 0,1 N solution.
7. Barium- diphenylamine sulphonate indicator
   - Dissolve 0,32 g of barium-diphenylamine sulphonate in 100 mL of distilled water.

8. Analytical Procedure

1. Mix sample thoroughly.
2. Transfer 10 mL of the sample to a tared beaker. Record the weight. (The weight of the sample will be used in the calculation of percent total iron.)
3. Transfer the sample to a 250 mL volumetric flask and make to the mark. Mix well.
4. Pipette 50 mL of sample from the 250 mL volumetric flask into a 500 mL Erlenmeyer flask.
5. Add 15 mL of concentrated sulphuric acid and 10 mL of concentrated hydrochloric acid to the flask.
6. Place the above flask onto a hotplate and bring to a boil.
7. When the above solution has reached boiling point. **Add stannous chloride solution drop by drop**, while gently swirling the flask with heat-resistant tongs until the yellow iron colour in the solution is discharged. **Add no more than one drop of stannous chloride solution in excess**.
8. Allow the solution to cool to room temperature, and add 10 mL of saturated mercuric chloride solution.
9. A white,silky precipitate should form. If a grey, black precipitate forms, this indicates an excessive amount of stannous chloride. Start again.

10. Dilute the white silky precipitated solution to 150 mL with distilled water. Add 15 mL of the sulphuric/phosphoric acid solution and 0,3 mL of the barium diphenylamine sulphonate indicator.
11. Titrate at once with 0,1 N potassium dichromate solution to a violet-blue end point.

9. Calculations

$$\% \text{ Total iron} = \frac{\text{mL of 0,1N } K_2Cr_2O_7 \text{ x 0,5585}}{\text{g of sample x 50/250}}$$

10. References

1. ANSI/AWWA B407-93

2.8.8. FERROUS (Fe^{2+}) ION CONTENT OF COMMERCIAL FERRIC CHLORIDE SOLUTION

1. Introduction

It is the ferric ion in ferric chloride solutions, which forms the ferric hydroxide precipitate during coagulation reactions. Therefore, the ferrous ion concentration of ferric chloride solutions should be low if the solution is to be effective. This method is for ferrous ion determination in ferric chloride in the liquid form.

2. Scope

This method maybe used to confirm the iron content of liquid ferric chloride solution thereby identifying the percentage of ferrous iron.

3. Interferences

4. Hazards

Contact with skin may cause irritation, wear gloves. Wear goggles as ferric chloride solution may cause burns to the eyes.

5. Sample Collection

Samples may be collected in plastic or glass containers.

6. Apparatus

1. Analytical balance
2. Volumetric flasks 1 L.
3. Measuring cylinders

7. Reagents

1. Concentrated sulphuric acid
2. Sulphuric acid/phosphoric acid solution
    - Into a 1 L volumetric flask add 500 mL of distilled water. To this water add 150 mL of sulphuric acid and 150 mL of 85% phosphoric acid, make up to 1 L. **Remember to pour acids into water.**
3. Potassium dichromate solution

- Dissolve 4,902 g of previously dried reagent grade potassium dichromate in distilled water. This is a 0,1 N solution.

4. Barium- diphenylamine sulphonate indicator
   - Dissolve 0,32 g of barium-diphenylamine sulphonate in 100 mL of distilled water or better quality.

8. Analytical Procedure

1. Use the same sample that was prepared for iron content or prepare sample as below.
2. Mix sample thoroughly.
3. Transfer 10 mL of the sample to a tared beaker. Record the weight. The weight of the sample will be used in the calculation of percent total iron.
4. Transfer the sample to a 250 mL volumetric flask and make to the mark. Mix well.
5. Pipette 100 mL of sample from the 250 mL volumetric flask into a 500 mL Erlenmeyer flask.
6. Add 15 mL of concentrated sulphuric acid.
7. Dilute to 200 mL with distilled water or of better quality.
8. Allow to cool to room temperature.
9. Add 15 mL of the sulphuric/phosphoric acid solution and 12 drops of the barium diphenylamine sulphonate indicator solution.
10. Titrate at once with 0,1 N potassium dichromate solution to a violet-blue end point.

9. Calculations

$$\% \text{ Ferrous iron} = \frac{\text{mL of 0,1N } K_2Cr_2O_7 \text{ x } 0.5585}{\text{g of sample x } 100/250}$$

% Ferric iron = % Total iron (from previous method 2.8.7) - % Ferrous iron

therefore % Ferric chloride = % Ferric iron x 2,905

10. References

1. ANSI/AWWA B407-93

FERRIC CHLORIDE

WORKSHEET 1

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

SPECIFIC GRAVITY/ DENSITY			
Sample 1	**Sample 2**	**Sample 3**	**Density**

BASICITY OR FREE ACID	
Mass of liquid Ferric chloride g	
Blank	
Titre 1	
Titre 2	
Titre 3	

TOTAL INSOLUBLE MATTER	
Mass of filter paper	
Weight of sample g	
Mass of filter paper + sample	
% Total Insolubles	

FERRIC CHLORIDE

WORKSHEET 2

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received laboratory	
Sample number	

TOTAL IRON CONTENT	
Mass of liquid Ferric chloride g	
Blank	
Titre 1	
Titre 2	
Titre 3	

FERROUS IRON CONTENT	
Mass of liquid Ferric	
Blank	
Titre 1	
Titre 2	
Titre 3	

2.8.9. SPECIFIC GRAVITY OF FERRIC SULPHATE

1. Introduction

The density of an object is described as its mass per unit volume. We express this as:

$$D = M/V$$

Since density is characteristic of a substance, it can be helpful in identifying it and determining whether a substance is pure, or the concentration of a substance in solution.

2. Scope

This method maybe used to confirm the density of a ferric sulphate solution thereby identifying the percentage of ferric sulphate.

3. Interferences

Temperature

4. Hazards

Corrosive, wear gloves when handling.

5. Sample Collection

Samples may be collected in plastic containers.

6. Apparatus

1. Analytical balance
2. Volumetric flasks 50 mL
3. Dropper pipettes

7. Reagents

None

8. Analytical Procedure

1. Place the volumetric flask on the balance and tare (zero).
2. Remove the flask from the balance and place on a clean dry surface.
3. Place a tiny funnel into the flask and carefully add the ferric to the flask with a dropper without obtaining any ferric on the sides.
4. Fill the flask to the 50 mL meniscus and return to the balance.
5. Record the weight.

9. Calculations

$$\text{Density} = \frac{\text{(reading on the balance)}}{50} \text{ (g/mL)}$$

In the case of a solution, the density (in g/mL) is numerically equal to the specific gravity (SG).
Refer to **Table 3** below for the conversion of SG to % ferric sulphate.

10. References

1. Umgeni Water South African National Accreditation Services method.
2. Ferric sulphate table from Sudchemie.

TABLE 2.3: S.G. of Commercial Ferrric Sulphate Solution (Sudchemie)

Specific Gravity	% Ferric Sulphate
1,04	1
1,08	2
1,12	3
1,17	4
1,23	5
1,28	6
1,35	7
1,41	8
1,48	9
1,56	10
1,64	11
1,72	12
1,81	13
1,90	14
2,00	15
2,09	16
2,20	17
2,31	18
2,42	19
2,54	20

2.8.10. SOLUBLE FERRIC ION (Fe^{3+}) CONTENT OF LIQUID FERRIC SULPHATE

1. Introduction

Ferric ion is the active ingredient in ferric sulphate solutions and therefore it is important to determine the concentration of ferric ion in ferric solutions. This method is for ferric ion concentration determination in ferric sulphate supplied in solution form

2. Scope

This method describes a procedure for the determination of Fe^{3+} content.

3. Interferences

None.

4. Hazards

Corrosive. When handling liquid ferric sulphate wear gloves, goggles and an acid resistant apron.

5. Sample Collection and Preservation

Samples may be collected in plastic containers.

6. Apparatus

1. 50 mL Burette
2. 250 mL glass stoppered bottle
3. Analytical balance
4. A grade glass pipettes

7. Reagents

1. 10% (m/v) Potassium Iodide Solution
2. 0,375 N Potassium Iodate (KIO_3) Solution
    - Dry about 25 g of KIO_3 at 120º C for one hour and allow to cool in a desiccator.
    - Accurately weigh 13,3751 g of potassium iodate and transfer quantitatively to a 1 L volumetric flask.

- Make up to volume with distilled water and mix well.

3. 0,15 N Sodium Thiosulphate Solution
   - Dissolve 37,277 g of sodium thiosulphate pentahydrate in distilled water and transfer to a 1 L volumetric flask.
   - Add 5 mL of chloroform and make up to volume with distilled water.
4. 25% (v/v) Sulphuric Acid (1:3 H_2SO_4)
   - Slowly add 100 mL of concentrated sulphuric acid to 300 mL of distilled water with constant stirring.
5. 0,5% (m/v) Starch Indicator Solution
   - Dissolve with heating 5 g of starch in distilled water. Allow to cool and make up to 1 L with distilled water.

8. Analytical Procedure

1. Accurately pipette 2 mL of ferric sulphate into a 250 mL glass stoppered bottle.
2. Dilute with distilled water to approximately 50 mL.
3. Add 12 mL of concentrated hydrochloric acid and 2 to 3 g of potassium iodide crystals.
4. Stopper and leave in the dark for 5 minutes.
5. Make up a blank using approximately 50 mL of distilled water, 12 mL of concentrated hydrochloric acid and 2 to 3 g of potassium iodide crystals.
6. Stopper and leave in the dark for 5 minutes.
7. Make up a standard using 10 mL of 0,375 N potassium iodate, 50 mL of distilled water, 10 mL of 25% sulphuric acid and 10 mL of 10% potassium iodide solution.
8. Titrate the standard, blank, and samples against 0,15 N sodium thiosulphate solution using starch as indicator. Colour change: blue – colourless.

9. Calculations

$$2Fe^{3+} + 2I^- = 2Fe^{2+} + I_2$$

$$\text{Ferric iron concentration g/L} = \frac{(V_1 - V_2) \times V_{STD} \times 55{,}84 \times N}{V_3 \times V_S}$$

$$= \frac{(V_1 - V_2) \times 10 \times 55{,}84 \times 0{,}375}{V_3 \times 2{,}00}$$

Where:

V_1 = volume (mL) of sodium thiosulphate solution used in the titration of the sample.

V_2 = volume (mL) of sodium thiosulphate solution used in the titration of the blank.

V_{STD}= volume of standard used for the tiration, in mL (in this method 10 mL used)

N = concentration of the sodium thiosulphate, equivalents per litre; (0,375 N)

V_3 = volume (mL) of sodium thiosulphate solution used in the titration of the standard.

V_s = volume (mL) of sample used for the titration (2 mL).

10. References

1. City of Cape Town method
2. AWWA standard method ANSI/AWWA B406-97

2.8.11. FERROUS ION (Fe^{2+}) CONTENT OF FERRIC SULPHATE

1. Introduction

When using ferric sulphate solutions in water and wastewater treatment, it is the ferric ion which is important in precipitation reactions. It is therefore important to ensure that the ferrous ion concentration is not too high.

2. Scope

This method describes a procedure for the determination of the ferrous ion content of ferric sulphate.

3. Interferences

Ferric sulphate is mildly hygroscopic and should therefore be stored in a dry place.

4. Hazards

Corrosive. Wwhen handling liquid ferric sulphate goggles, gloves, and an acid resistant apron should be used.

5. Sample Collection and Preservation

Samples may be collected in plastic containers.

6. Apparatus

1. 50 mL Burette
2. 250 mL conical flasks
3. Analytical balance
4. A grade glass pipettes

7. Reagents

1. 25% v/v Phosphoric Acid
   - Add 25 mL of phosphoric acid to 75 mL distilled water.
2. Barium diphenylamine sulphonate indicator
   - Dissolve 1,0 g of barium diphenylamine sulphonate in distilled water and make to 100 mL.
3. 0,03 N Potassium dichromate solution ($K_2Cr_2O_7$)

- Dry about 25 g of $K_2Cr_2O_7$ at 120º C for one hour and allow to cool in a desiccator.
- Accurately weigh 14,7105 g of $K_2Cr_2O_7$ and transfer quantitatively to a 1 L volumetric flask.
- Make up to volume with distilled water and mix well.

8. Analytical Procedure

1. Pipette out 2,00 mL of ferric sulphate into a conical flask.
2. Add 15 mL of concentrated Hydrochloric acid and 50 mL distilled water.
3. Add 30 mL of 25% v/v phosphoric acid.
4. Add 9 drops of barium diphenylamine sulphonate indicator solution.
5. Titrate with 0,03 N $K_2Cr_2O_7$ to an intense purple or violet blue colouration persists.

9. Calculation

The equation for the reaction is:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^{+} = 2\ Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Therefore: Ferrous Iron Fe^{2+} g/L $= \dfrac{V_1 \times 0{,}01675 \times 1\,000}{V_s \times 10}$

$= \dfrac{V_1 \times 0{,}01675 \times 100}{2{,}00}$

Where:

V_1 = volume of potassium dichromate used in the titration of the sample (mL).

V_s = volume of sample used for the titration (mL); (in this case 2 mL).

10. References

1. City of Cape Town Methods

2.8.12. ALTERNATIVE TESTS FOR FERROUS (Fe^{2+}) IRON IN FERRIC SULPHATE

1. Introduction

As mentioned in the previous method, it is the ferric ions in ferric sulphate which are the active ions in precipitation and phosphate removal reactions and for this reason it is important to limit the amount of ferrous ions present in ferric sulphate solutions. This method provides an alternative method for determining the ferrous ion content of ferric sulphate solutions.

2. Scope

This method describes a procedure for the determination of the soluble ferrous iron content of ferric sulphate.

3. Interferences

Ferric sulphate is mildly hygroscopic and should therefore be stored in a dry place.

4. Hazards

Corrosive. When handling liquid ferric sulphate, goggles, gloves and an acid resistant apron should be used.

5. Sample Collection and Preservation

Samples may be collected in plastic containers.

6. Apparatus

1. 100 mL volumetric flask
2. Burette
3. Conical flasks

7. Reagents

1. 0,01 N Ceric sulphate $Ce(HSO_4)_4$
   - Measure out 500 mL of distilled water and add 30 mL of sulphuric acid (add slowly while stirring).
   - To the acidified water add 5,28 g of ceric sulphate and dilute to 1 L.

2. Ortho-phenanthroline indicator solution
3. 1:1 Hydrochloric acid solution

8. Analytical Procedure

1. Weigh 20 g (± 0,001 g) of the sample and transfer into a 100 mL volumetric flask.
2. Dilute to the volume mark with distilled water and mix. Thoroughly shake sample.
3. Pipette 10 mL of the above solution into a conical flask.
4. Add 80 mL of distilled water and 5 mL of hydrochloric acid.
5. Titrate against 0,01 N Ceric sulphate, using ortho-phenanthroline as an indicator.
6. Run a blank sample of 50 mL of distilled water using the same amount of indicator solution.

9. Calculations

Report the results as percentage water-soluble ferrous iron in the solution.

$$\% \text{ water soluble } Fe^{2+} = \frac{(\text{mL ceric sulphate - blank}) \times (\text{N ceric sulphate}) \times 0{,}05585 \times 10 \times 100}{\text{weight of sample* in grams}}$$

* Weight from 8.1

10. References

1. AWWA ANSI/AWWA B406-97

FERRIC SULPHATE QUALITY CONTROL

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

SPECIFIC GRAVITY/ DENSITY			
Sample 1	**Sample 2**	**Sample 3**	**Density**

SOLUBLE FERRIC IRON CONTENT	
Blank	
Titre 1	
Titre 2	
Titre 3	
Ferric iron g/L	

SOLUBLE FERROUS IRON CONTENT	
Blank	
Titre 1	
Titre 2	
Titre 3	
Ferrous iron g/L	

2.8.13. MOISTURE CONTENT OF GRANULAR FERRIC SULPHATE

1. Introduction

Ferric sulphate is used as an inorganic coagulant for removal of suspended and colloidal particles from water and wastewater by coagulation and flocculation. It is also used in wastewater for phosphate removal. It is prepared by oxidising ferrous sulphate or by dissolving ferric oxide in sulphuric acid. With granular forms of this coagulant, high moisture content is undesirable.

2. Scope

This method describes a procedure for the determination of the moisture content of ferric sulphate.

3. Interferences

Ferric sulphate is mildly hygroscopic and should therefore be stored in a dry place.

4. Hazards

Corrosive. When handling liquid ferric sulphate use goggles, gloves and an acid resistant apron.

5. Sample Collection and Preservation

Samples may be collected in plastic containers.

6. Apparatus

1. Porcelain dish
2. Desiccator

7. Reagents

None

8. Analytical Procedure

1. Weigh porcelain dish and record the mass. (M1)
2. Weigh 10 g of the ground ferric sulphate sample into porcelain dish and record mass (M2).

3. Dry for 5 hours at 100º C oven.
4. Allow to cool in a desiccator and weigh and record weight (M3).

9. Calculations

$$\% \text{ Moisture} = \frac{(M2 - M3) \times 100}{M2 - M1}$$

10. References

1. AWWA ANSI/AWWA B406-97

2.8.14. SAMPLE PREPARATION AND SIEVE ANALYSIS FOR GRANULAR FERRIC SULPHATE

1. Introduction

Granular ferric sulphate is prepared by oxidising ferrous sulphate or by dissolving ferric oxide in sulphuric acid. It is used in both water and wastewater as a coagulant and it is also used in wastewater for phosphate removal. According to the ANSI/AWWA B406-97 Standard for Ferric Sulphate, when supplied in the dry form, ferric sulphate should be fairly uniform in size, and not less than 95% should pass through a 4,75 µm screen (No. 4 US Standard Sieve).

2. Scope

This method describes a procedure for the sample preparation and sieve analysis of ferric sulphate.

3. Interferences

Ferric sulphate is mildly hygroscopic and should, therefore, be stored in a dry place.

4. Hazards

Corrosive. When handling liquid ferric sulphate use goggles, gloves, and an acid resistant apron.

5. Sample Collection and Preservation

Samples may be collected in plastic or glass containers.

6. Apparatus

1. Riffler
2. Sieves
3. Pestle and mortar

7. Reagents

None

8. Analytical Procedure

1. Riffle or quarter the sample to provide two samples, one sample of 150-200g for physical sieve analysis and the second of about 100g for chemical analysis.
2. After thorough mixing, store the 100g sample for chemical analysis in an airtight glass container and weigh out rapidly to avoid a change in moisture content.
3. Grind approximately 50g of the 100g sample to such a size that all of it passes through a 180µm (No. 80 US Standard) sieve. Place this ground sample in an airtight container until required for analysis.
4. Quantitatively transfer the 150g-200g sample to a set of sieves composed of a 5,60 µm (No. 3 US Standard) sieve and a 4,75 µm (No. 4 US Standard) sieve and a pan.
5. Sieve by lateral and vertical motion accompanied by a jarring action. Continue for about 5 minutes or until an additional 3 minutes of sieving time fails to change the results of any sieve fraction by 0.5% of the total sample weight.
6. 100% should pass through the 5,60 µm (No. 3 US Standard) sieve and not less than 95% should pass through the 4,75 µm (No. 4 US Standard) sieve.

9. References

1. AWWA ANSI/AWWA B406-97

GRANULAR FERRIC SULPHATE QUALITY CONTROL

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

MOISTURE CONTENT			
Mass 1	**Mass 2**	**Mass 3**	**% Moisture**

SOLUBLE FERRIC IRON CONTENT	
Blank	
Titre 1	
Titre 2	
Titre 3	
Ferric iron g/L	

SIEVE GRADING				
Sieve	**Mass 1**	**Mass 2**	**% Retained**	**% Passing**

3. COAGULANT AIDS

3.1. INTRODUCTION

The use of coagulants to destabilise the colloidal material in water and form a settleable floc is often not completely successful and additional chemicals or compounds need to be added to assist the coagulation process. These may be added for a number of purposes which will become apparent when the chemicals listed below are discussed.

3.2. BENTONITE

Bentonite and kaolin are naturally occurring clays, which are added to water when the turbidity of the raw water is so low that adequately weighted flocs cannot be produced. Bentonite is the more frequently used, although the effects of both are similar. Normal procedure is to add bentonite to the raw water prior to the addition of the coagulant so that it adds weight to the resulting floc. Dosages of bentonite are often quite low being of the order of 1 to 5 mg/L. Although bentonite can be added using dry screw feeders, this is not usually successful as insufficient time elapses for the clay to become adequately hydrated. Normal practice is to prepare an approximately 5% suspension (50g/L) and to add this by means of positive displacement dosage pumps. Bentonite does not modify the pH or the chemical characteristics of the water apart from providing additional weight to the floc which is formed.

3.3. SODIUM ALUMINATE

Sodium aluminate has the formula $Na_2O.Al_2O_3.H_2O$ and is an alkaline form of soluble aluminium. Sodium aluminate is a coagulant in its own right and on certain types of water produces good results when used as a coagulant on its own, rather than as a coagulant aid. The sodium aluminate reacts with the bicarbonate or carbon dioxide in the water to give an aluminium hydroxide floc which coagulates in the normal way. Its use is preferred in waters that coagulate better at relatively high pH's although this is not always the case.

Sodium aluminate is also used as a floc aid, under certain circumstances the addition of sodium aluminate together with aluminium sulphate produces large flocs that coagulate and settle well. Sodium aluminate is available as a commercial reagent containing approximately 50% Al_2O_3 and is dosed at concentrations ranging from approximately 5 to 50 mg/L depending on the application. The higher dosages are generally employed when it is used on its own and lower dosages when used in combination with aluminium sulphate. Unlike nearly all other coagulants, sodium aluminate increases the pH of the water as it contains free alkalinity. The use of aluminium sulphate and sodium aluminate in combination can therefore be used where the pH of the water needs to be held reasonably constant.

3.4. ACTIVATED SILICA

Activated Silica is a floc aid that increases the weight and size of flocs formed after the addition of the coagulant. It is prepared by acidification of sodium silicate which has the formula $SiO_2.Na_2O$. Sodium silicate is supplied as a viscous solution with a specific gravity of between 1,35 and 1,4 at a concentration of 24 to 28%. Preparation of activated silica involves several stages, these being acidification of the concentrated sodium silicate solution, ageing for a definite time and dilution of the resulting solution. Suitable acids for acidification and neutralization of part of the alkalinity are sulphuric acid, hydrochloric acid, aluminium sulphate, sodium bicarbonate and hypochlorous acid (aqueous chlorine). The supplier of the sodium silicate solution, frequently states the conditions for acidification, ageing and dilution. For laboratory purposes, approximately 31 mLs of 29% sodium silicate solution can be diluted to 1litre to yield a 1,25% SiO_2 solution. 80 mLs of this solution, when added to a 100 mL volumetric cylinder and acidified with HCl to lower the pH to 5 and diluted to 100 mLs, gives a 1,0% SiO_2 solution which should be aged or activated for 30 minutes before being used directly as a coagulant aid. The dosage of activated silica when used under normal practice as a coagulant aid on a plant, is usually within the range of 0,5 to 4 mg/L as SiO_2.

3.5. POLYELECTROLYTES

Whereas the polyelectrolytes used as primary coagulants are generally cationic and usually polyamines of molecular weight in the range of 750 000, or Dimethyldiallyl

ammonium chloride (DIMDAACS) products with a molecular weight of up to 1,5 million, the polyelectrolytes used as coagulant aids are anionic or non-anionic polyacrylamides with molecular weights of up to 10 million.

The polyacrylamides are usually supplied as granular solids and are difficult to dissolve. For plant use, the suppliers of these chemicals often provide eductors that draw the granules into the mixing water stream in a thin stream and distribute it widely in the mixing tank. It is then mixed for a considerable period of time, usually lasting several hours, and the solution is then aged for up to 24 hours before use. The dissolution of polyacrylamides in water is slow and the ageing period is necessary for complete solubilisation to take place. Because of the long molecular chains these need to be unbundled for full activity to be achieved. If the polyacrylamide is not carefully mixed, it forms large lumps in the water, which partially hydrate giving rise to “fish eyes” which then do not go into solution and can block the dosage pumps.

The polyacrylamides are normally prepared as a 0,2% (2 g/L) solution which even at such low concentrations is relatively viscous. The solid material is relatively inert although protective equipment should be used when handling it and it has a relatively low bulk density.

The polyacrylamides are added to the water as floc aids at concentrations as low as 0,05 to 0,1 mg/L. Although slightly higher concentrations may be acceptable where the coagulant dose is relatively high (typically 100 mg/L of aluminium sulphate), care should be taken to avoid the temptation to add excessive quantities of polyacrylamides because although these produce excellent flocs the excess polymer remaining in solution can rapidly cause blockages on the rapid gravity filters.

3.6. EVALUATION OF COAGULANT AID CHEMICALS

As with all process chemicals, selection criteria are required in order to choose the best product in terms of performance and cost effectiveness. Having done this, it is important that the quality of the product remains consistent and does not deteriorate relative to the original product, which means that regular quality control testing of each delivery of the chemical will be required. In some cases the testing used for selection of product is far more rigorous than that used for quality control monitoring. For most of the coagulant aid chemicals described in this manual, the test protocol for product selection is similar to that used for quality control monitoring, although in the case of polyacrylamides, jar test type tests and plant trials are recommended during the selection process.

3.6.1. BENTONITE

The most important aspect of bentonite in terms of quality control and operation is the grit content. A high grit content can result in damage to pumps and feed impellers and in order to prevent damage from occurring to equipment, the grit content should not exceed 5% The grit content of bentonite is determined by measuring the residue retained on a 53 µm sieve. This test is generally adequate for both selection and quality control testing of bentonite, although jar tests can also be used in the selection process. Jar tests simulating the conditions on the plant as closely as possible and using different dosages of bentonite can be used for both comparison of different bentonite samples and for bentonite dose selection (see the Standard Jar Test procedure described in Section 2.6.1).

3.6.2. SODIUM ALUMINATE

Sodium aluminate is supplied in solid form. Apart from bulk density, there is no simple test to determine its quality or concentration of active ingredient. Although tests exist to measure aluminium colorimetrically or by atomic adsorption, these are relatively complex.

3.6.3. ACTIVATED SILICA

Activated silica is generated on site from sodium silicate and usually sulphuric acid. The quality of the sodium silicate can be checked by measuring either the specific gravity or the viscosity of the solution as supplied. The concentration of the sodium silicate solution should be agreed upon between the purchaser and the supplier,

although it is usually supplied as a solution with a concentration of between 24 and 28% and a specific gravity of between 1,35 and 1,4. The viscosity can be determined using a viscometer and density can be measured either by weighing a measured volume of the solution, or by using an appropriate hydrometer.

3.6.4. POLYACRYLAMIDES

There are not many simple tests available for the evaluation of polyacrylamides. For purposes of tender evaluation or product selection a Standard Jar Test procedure (see Section 2.6.1) can be used in which the conditions on the plant are simulated as closely as possible, including coagulant dose and addition of other process chemicals, and increasing polyacrylamide doses are used. These tests can be used both to optimise the coagulant aid dose and for purposes of comparing different products. Tests for bulk density, bulk viscosity, molecular weight and charge density can be performed and these are useful for quality control monitoring of different delivery batches.

3.7. ANALYTICAL METHODS

3.7.1. PERCENTAGE GRIT IN BENTONITE

1. Introduction

The grit content of bentonite needs to be minimised in order to avoid damage occurring to pumps and feed equipment. Ideally, the grit content should not exceed 5% when the bentonite is passed through a 53 µm sieve.

2. Scope

This method describes a procedure for the determination of percentage grit content in bentonite.

3. Interferences

4. Hazards

Dust.

5. Sample Collection and Preservation

Samples may be collected in either plastic or glass containers or packets.

6. Apparatus

1. High -speed blender.
2. Analytical balance.
3. Evaporating dish or metal crucible.
4. Sieve of pore size 53 µm

7. Reagents

1. Di - Sodium Dihydrogen Pyrophosphate ($Na_2H_2P_2O_7$), AR grade.

8. Analytical Procedure

1. Record the mass of the empty crucible or evaporating dish.
2. Weigh out 50,0 g of bentonite into a 500 mL glass beaker and to it add 300,0 mL of distilled water. Add approximately 5 g of di-sodium dihydrogen pyrophosphate and mix at a high speed until the solution is well blended.
3. Brush the suspension through a 53 μm sieve with a fine stream of water. Continue brushing until the water passing through the sieve is clear.
4. Transfer the residue retained on the sieve to a metal crucible or evaporating dish and dry to a constant mass. Record the mass of the residue.

9. Calculations

$$\% \text{ Grit} = \frac{(M1 - M2)}{50} \times 100$$

Where:

M1 = mass of empty dry crucible or dish (g).

M2 = mass of crucible or dish plus dry residue (g).

Sources of Error

Ensure that the water pressure is not too high as to splash some of the suspension out of the sieve.

10. References

1. Process Services, Umgeni Water.

BENTONITE

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

% GRIT			
Mass 1	**Mass 2**	**Mass 3**	**% Grit**

3.7.2. MEASURING THE DENSITY OF SODIUM SILICATE

1. Introduction

The density of an object is described as its mass per unit volume, i.e. D = M/V. Since density is characteristic of a substance, it can be used for determining the concentration of a solution.

2. Scope

This method may be used to measure the density sodium silicate either by weighing a measured volume of the solution, or using a suitable hydrometer.

3. Interferences

Temperature

4. Hazards

None

5. Sample Collection

Samples may be collected in glass or plastic containers.

6. Apparatus

Mass and Volume Method:

1. Analytical balance
2. Volumetric flasks 50 mL
3. Dropper pipettes

Hydrometer Method:

4. Suitable hydrometer

7. Reagents

None

8. Analytical Procedure

Mass and Volume Method:

1. Place the volumetric flask on the balance and tare (zero).
2. Remove the flask from the balance and place on a clean dry surface.
3. Place a tiny funnel into the flask and carefully add the sodium silicate solution to the flask with a dropper without obtaining any solution on the sides.
4. Fill the flask to the 50 mL meniscus with sodium silicate solution and return to the balance.
5. Record the weight.

Hydrometer Method:

6. Alternatively, use a suitable hydrometer, place in the solution, allow to stabilise and measure density off the graduated stem.
7. Measure the temperature of the solution and correct the hydrometer reading for temperature.

9. Calculations

Mass and Volume Method:

$$\text{Density} = \frac{\text{mass of sodium silicate in flask}}{\text{volume of flask}}$$

Hydrometer Method:

Adjust hydrometer reading for temperature.

10. References

1. "Standard Methods for the Examination of Water and Wastewater", 20th Edition, Edited by Greenberg, A. Pub. AAWA.
2. Process Services, Umgeni Water.

3.7.3. MEASURING THE VISCOSITY OF SODIUM SILICATE

1. Introduction

Viscosity is a measure of the ability of a liquid to resist various internal and external movements, such as flow. Viscosity can be affected by the concentration of an active ingredient present in a solution and can therefore be a good quality control indicator, indicating consistency in the product and whether changes, which may affect the activity of the coagulant, might have occurred.

2. Scope

This method may be used to determine the viscosity of sodium silicate.

3. Interferences

Temperature.

4. Hazards

None

5. Sample Collection

Samples may be collected in either glass or plastic containers.

6. Apparatus

1. Viscometer, Brookfield, Model LVT or equivalent.
2. Tall form 250 mL beaker

7. Reagents

1. Distilled water

8. Analytical Procedure

1. Set up the viscometer and level the instrument.
2. Attach the spindle specified by the polymer supplier. (NOTE: Left-handed threads.)
3. Pour enough sodium silicate solution into the beaker to cover the spindle up to the groove.

4. Lower the viscometer with the spindle attached into the sample until the surface of the sample meets the groove on the spindle shaft. The spindle should not touch the bottom of the beaker.
5. Set the viscometer to chosen revolutions per minute.
6. Turn on the viscometer motor.
7. After the needle reaches a steady reading, and after at least 10 revolutions, depress the clutch lever on the back of the viscometer to “freeze” the needle on the scale.
8. With the clutch depressed, stop the viscometer motor when the needle is visible in the viscometer window.
9. Read and record the position of the needle on the scale.
10. Repeat the procedure until you have three readings.
11. If the manufacturer does not specify a spindle start with spindle number 1 and follow the procedure. If the needle is not near the middle of the of the viscometer’s scale range, use the next spindle size up and repeat until a correct reading has been obtained.

9. Calculation

Average the three readings.

Obtain the Brookfield viscosity by multiplying the average reading calculated by the factor for that spindle and speed supplied by the viscometer manufacturer.

10. References

1. ANSI/AWWA B451-98

SODIUM SILICATE

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

DENSITY			
Sample 1	**Sample 2**	**Sample 3**	**Density**

VISCOSITY			
Spindle	**Viscometer reading**	**Factor**	**Viscosty**
Average			

3.7.4. ALKALINITY DETERMINATION OF SODIUM ALUMINATE

1. Introduction

Alkalinity is a measure of the ability of a water to neutralise acids and bases. For sodium aluminate, it can be used to confirm the quality of a solution.

2. Scope

This method may be used to determine the total alkalinity of sodium aluminate powder.

3. Interferences

4. Hazards

Hydrochloric acid: ensure that you are familiar with the dangers and treatment associated with each of the above substances.

5. Sample Collection

Samples may be collected in either bags or plastic containers.

6. Apparatus

1. Burette
2. Volumetric equipment.
3. A-grade glassware.

7. Reagents

Use only distilled water.

All prepared solutions are made up in volumetric flasks and are stored in glass containers, unless otherwise indicated.

1. Sodium carbonate (anhydrous AR grade).
2. 0,1N Hydrochloric acid
    - Add 8,9 mL of Hydrochloric acid to a 1 L volumetric flask and make to the mark using distilled water.
3. Phenolphthalein

- Dissolve 0,5g of phenolphthalein in 50 mL of methanol or ethanol, then dilute to 100 mL with water. Filter if necessary.

4. Methyl orange indicator
   - Prepare a 0,2% solution of methyl orange in 50% alcohol.
   - Colour change: yellow – orange – red.
5. Screened methyl orange indicator
   - Mix equal volumes of a 0,2% solution of methyl orange and 0,3% solution of xylene cyanol FF. Both are prepared in 50% alcohol.
   - Colour change: green – grey – red.

8. Analytical Procedure

1. Standardization of 0,1N HCl.
   - Accurately weigh 1,325 g of anhydrous sodium carbonate (AR grade previously heated to 260º C for 2 hours and cooled in a desiccator) into a 250 mL volumetric flask. Dissolve in distilled water and then dilute to the mark.
   - Actual normality of the standard sodium carbonate solution can be calculated as follow:

$$N_1 = \frac{\text{mass } Na_2CO_3 \text{ x } 4}{53}$$

   - Titrate 25 mL portions of this solution with 0,1N HCL solution using screened methyl orange as indicator. The colour change is green to grey to violet endpoint.
   - The concentration of the HCl solution can be calculated as follows:

$$\text{N HCl} = \frac{25 \text{ x } N_1}{\text{volume HCl (ml)}}$$

2. If testing sodium aluminate containing approximately 35% as Na_20, accurately weigh between 3 and 5 g and record the mass.
3. Transfer to a 250 mL conical flask containing approximately 50 mL of distilled water.
4. Add 4 drops of phenolphthalein indicator.
5. Titrate against 0,1N HCl to the first disappearance of the pink colour. Record this volume as Vp.

6. To the same flask, now add 4 drops of methyl orange or screened methyl orange indicator and titrate to the end point colour of the indicator. Record this volume as Vm.

9. Calculation

Calculation of phenolphthalein (hydroxide) alkalinity:

$$\% \text{ P Alkalinity as NaOH} = \frac{\text{Vp (mL) x N HCl x 40}}{\text{10 x mass (g)}}$$

$$\% \text{ M Alkalinity as } Na_2CO_3 = \frac{\text{Vm (mL) x N HCl x 53}}{\text{10 x mass (g)}}$$

$$\% \text{ Total Alkalinity as } Na_2CO_3 = \frac{\text{(Vp + Vm) x N HCl x 53}}{\text{10 x mass (g)}}$$

10. References

1. British standard specification for sodium carbonate. B.S. 3674:1963
2. British standard for Photography – Processing Chemicals - Specifications for sodium hydroxide. B.S. ISO 3617:1994.
3. “Standard Methods for the Examination of Water and Wastewater”, 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.

SODIUM ALUMINATE

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

STANDARDISATION 0,1N HCL	
Mass sodium Carbonate	
Titre 1	
Titre 2	
Average	

ALKALINITY mg/L $CaCO_3$	
Mass of Na_2O in g:	**Titre :**
Mass of Na_2O in g:	**Titre:**
Mass of Na_2O in g:	**Titre:**

3.7.5. BULK DENISTY OF POLYACRYLAMIDE

1. Introduction

The bulk density is defined as the mass of a unit volume of the sample in air in kg/m^3.

2. Scope

This method can be used to determine the bulk density of powder or granular polyacrylamide.

3. Interferences

4. Hazards

None.

5. Sample Collection

Samples may be collected in either bags or plastic containers.

6. Apparatus

1. Volumetric cylinder
2. Electronic balance

7. Reagents

None

8. Analytical Procedure

1. Weigh a dry volumetric cylinder, M1 (g).
2. Fill this cylinder with the powder and shake gently to remove air pockets.
3. Measure the powder volume, V (mL), and weigh the cylinder containing the polymer, M2 (g).

9. Calculation:

$$\text{Bulk density} = \frac{M2 - M1}{V} \text{ kg/m}^3$$

10. References

1. Rand Water Method.

3.7.6. BULK VISCOSITY OF POLYACRYLAMIDE

1. Introduction

The bulk viscosity can be determined on polyacrylamide supplied in solution form. Emulsion or solution forms of polyacrylamide typically have a bulk viscosity range of 200 to 4 000 centipoises, although they are not limited to this range and it certainly is not a specification for these products. This test can be used though to confirm consistency of product between different deliveries or batch productions.

2. Scope

This method can be used to determine the bulk viscosity of emulsion or solution forms of polyacrylamide.

3. Interferences

4. Hazards

None.

5. Sample Collection

Samples may be collected in either glass or plastic bottles.

6. Apparatus

1. 1 L screw top bottles
2. Brookfield Viscometer

7. Reagents

None

8. Analytical Procedure

1. Pour 250 mL of 0,5% polymer solution into a dry, clean 1 L screw top bottle.
2. Place bottle with sample in constant temperature bath at 20°C.
3. Allow sample temperature to equilibrate.
4. Measure viscosity with a Brookfield viscometer after thorough mixing.
5. Use suitable spindle at 30 rpm.

9. Calculation

Viscosity = viscometer reading x factor (centipoises at 20°C)

10. References

1. AWWA Standard for Polyacrylamide, ANSI/AWWA B453-96.

3.7.7. CHARGE DENSITY OF POLYACRYLAMIDE

1. Introduction

The charge density affects the way in which a polyacrylamide reacts. It can also be used as a quality control parameter as it should remain fairly consistent between deliveries of product.

2. Scope

This method is a simple titration procedure that allows determination of the charge density of a polyacrylamide.

3. Interferences

4. Hazards

None.

5. Sample Collection

Samples may be collected in bags, glass or plastic bottles.

6. Apparatus

1. 1 L Volumetric flasks
2. 100 mL Volumetric flasks
3. 1 L Glass bottles
4. Magnetic stirrer and stirrer bar.
5. Buchner filter
6. Whatman No. 41 filter papers.
7. 50 mL Burette
8. 250 mL Erlenmeyer flasks

7. Reagents

1. 1,5–Dimethyl–1,5–diazaundecamethylene polymethobromide (DDPM), (0,0002N).

- Weigh [0,0374 x 100 / % purity] (g) DDPM and make up to 1 L with deionised water in a 1 L volumetric flask.
- Stir for approximately two hours.
- Transfer contents to a clean labelled bottle.
- The solution will last for two to five days.

2. Polyvinyl sulphate, potassium salt (PVSK) (0,001 N)
    - Place 1 g of PVSK into a 1 L volumetric flask and dilute to 1 L using distilled deionised water.
    - Stir overnight using a magnetic stirrer at maximum speed.
    - Filter the entire solution through Whatman 41 under vacuum and then through a Gelman A&E type filter paper under vacuum.
    - Place filtered solution in clean, labeled bottle.
3. Toluidine blue O (TBO) [0,1% solution (m/v)]
    - Add 0,1 g TBO into a 100 mL volumetric flask.
    - Dilute to 100 mL with deionised water.
    - Transfer to labeled bottled after thorough mixing.
    - Reagent is stable for six months.

8. Analytical Procedure

1. Standardisation of PVSK with DDPM
    - Fill a 50 mL burette with PVSK solution.
    - Place 10 mL DDPM reagent, two drops TBO indicator and a magnetic stirrer bar into a 300 mL flask.
    - Add incremental volumes of PVSK solution allowing a few seconds for equilibration between additions.
    - At the titration end point the colour changes from blue to light purple.
    - Determine a blank by replacing the 10 mL DDPM reagent with 10 mL distilled or deionised water.
2. Determination of normality of polymer
    - Fill a burette with standardized PVSK solution.
    - The titration mixture contains:
    - 1,0 mL 0,05% polymer solution (m/v)
    - 10,0 mL DDPM standard.
    - 2 drops TBO indicator.
    - Add distilled water, ± 20 mL

- Titrate until purple end point is reached.
- Determine blank by titrating 10 mL DDPM without polymer.

9. Calculation

1. PVSK solution normality calculation.

$$N_1 = \frac{V_2 N_2}{V_1}$$

Where:

N_2 = normality DDPM standard

V_2 = volume (mL) of DDPM titrated

V_1 = average volume (mL) of PVSK titrant consumed

N_1 = normality of PVSK

2. Charge Density

A = B - C

Where:

A = Negative charge on polymer

B = Average volume PVSK required to titrate 10 mL DDPM

C = Average volume PVSK required to titrate 10 mL DDPM – polymer

$$\text{Normality of polymer (N)} = \frac{\text{A x N (PVSK titrant)}}{\text{Volume polymer titrated (mL)}}$$

$$\text{Charge density (g/eq)} = \frac{\text{M (g/L)}}{\text{N (eq/L)}}$$

Where:

M = Mass polymer (0,5 g) per litre

N = Normality of polymer

10. References

1. Rand Water Method.

3.7.8. MOLECULAR WEIGHT OF POLYACRYLAMIDE

1. Introduction

The molecular weight of a polyacrylamide should remain fairly consistent between deliveries of product. Performance of the product may be linked to the molecular weight, so this analysis of the parameter can be used for quality control monitoring.

2. Scope

This method can be used to determine the molecular weight of a polyacrylamide. The method involves determination of both the solid content and the specific gravity of the polyacrylamide in order to calculate the molecular weight.

3. Interferences

4. Hazards

None.

5. Sample Collection

Samples may be collected in bags, glass or plastic bottles.

6. Apparatus

1. Weighing dish (aluminium, stainless steel, porcelain or platinum)
2. Electronic balance
3. Oven at 120 ± 5°C
4. Beakers
5. 100 µm Screen
6. Volumetric flasks (1 L and 100 mL)
7. Viscometer

7. Reagents

1. Citric acid
2. Di-sodium hydrogen phosphate
3. Sodium chlorite
4. 1 M NaCl pH 7 dilution buffer

- Place 1,335 g citric acid, 26,6 g di-sodium hydrogen phosphate and 116,9 g sodium chloride into a 1 L volumetric flask and dilute to the mark with distilled water.

8. Analytical Procedure

Determination of the solid content

1. Weigh an aluminium dish to at least the nearest 0,001 g and record as M1 (g).
2. Add 10 g sample and weigh again. Record this weight as M2 (g).
3. Place sample in oven at 120° C and allow sample to dry two hours.
4. Remove sample from oven and allow to cool to room temperature in a desiccator containing silica gel.
5. Weigh the dish containing dried powder. Record as M3 (g).

Determination of the specific viscosity:

6. Dissolve the equivalent of 1 g of dry content polymer into 100 mL deionised water (1% polymer solution).
7. Stir until completely dissolved.
8. Filter through 100 µm screen
9. Weigh 4, 6, 8 and 10 g of 1% polymer solutions into separate 100 mL volumetric flasks.
10. Add 50 mL 1M NaCl pH 7 dilution buffer to each and mix thoroughly.
11. Make up to 100 mL each with distilled water.
12. Use 50 mL 1M NaCl pH 7 dilution buffer solution made up to 100 mL with distilled water in a volumetric flask as the blank.
13. Allow a clean, dry viscometer tube or a suitable beaker to stand in a constant temperature bath at 30° C for at least ten minutes before measuring flow times t_o for blank and t for different polymer solutions.
14. Repeat flow time measurements until figures for the same dilution agree within 1%.
15. The intrinsic viscosity is obtained by plotting the viscosity number (Vred, see calculation), against polymer concentration and reading the value of the intercept with the Y-axis.

9. Calculation

Solids content:

$$\text{Solids content} = \frac{M3 - M1}{M2 - M1} \times 100\%$$

Specific Viscosity:

$$\text{Specific viscosity (Vsp)} = \frac{V - V_O}{V}$$

$$= \frac{t - t_o}{t_o}$$

Where:

V = Viscosity of polymer solution

V_o = Viscosity of blank

t = Flow time of polymer solution

t_o = Flow time of blank

(a) Calculate the viscosity number for polymer solution

$$\text{Vred} = \frac{\text{Vsp}}{C}$$

Where:

C = concentration of polymer solution.

$$\text{Vred} = \frac{t - t_o}{t_o} \times \frac{1}{C}$$

(b) Plot Vred as a function of C

(c) Read off the intercept at C = O

This is intrinsic viscosity value

Mean molecular weight can be obtained using the following formula:

$IV = 3,73 \times 10^{-4} \times Mw^{-0,66}$

Where:

IV = intrinsic viscosity

Mw = average molecular weight

10. References

1. Rand Water Method.

POLYACRYLAMIDE WORKSHEET 1

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

BULK DENSITY			
Sample	**M1**	**M2**	**Bulk density kg/m^3**

BULK VISCOSITY	
Spindle number + factor	**Viscometer reading**

CHARGE DENSITY			
Standardisation of PVSK		**Normality of polymer**	
Titre 1		**Titre 1**	
Titre 2		**Titre 2**	
Titre 3		**Titre 3**	
Blank		**Blank**	
		Mass of polymer g	

POLYACRYLAMIDE SHEET 2

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

MOLECULAR WEIGHT			
Determination of Solids Content			
Mass A	**Mass B**	**Mass C**	**% Solids content**

SPECIFIC VISCOSITY				
Determination of Specific Viscosity				
Mass 1% poly	**Concentration mg/L**	**Flow time**	**Viscosity**	**Viscosity number**
Blank (0)	**0**			
4	**4**			
6	**6**			
8	**8**			
10	**10**			

4. SLUDGE TREATMENT COAGULANTS

4.1 INTRODUCTION

Waterworks sludge consists of the suspended solid material that occurs in raw water together with the precipitated chemicals used to bring about the separation of the suspended solids (Sanks, 1978). The nature of the sludge is dependent on both the raw water quality as well as the types of chemicals and dosages used in the treatment process. For example, the sludges formed when using aluminium sulphate for coagulation tend to be colloidal and sticky and are often difficult to thicken or dewater mechanically (Sanks, 1978). In contrast, the sludges produced during lime-soda ash softening treatment are generally dense, stable and inert and dry well.

The quantity of sludge produced can be calculated using a solids balance and the relevant chemical equations for any of the reactions that take place due to the addition of treatment chemicals (Water Quality and Treatment, 1990). However, the largest contributor to the volume of sludge produced during water treatment is usually the turbidity or suspended solids of the raw water (Sanks, 1978) and tables are available which list the theoretical sludge production for the various types of matter which cause turbidity. It is therefore possible to calculate the kilograms of solids that will be produced by 1 kilogram of treatment chemical added for a particular raw water quality (Water Quality and Treatment, 1990).

Sludges are produced not only during the treatment of potable water, but also in the treatment of industrial effluents and sewage effluent. Various methods of sludge disposal are used. The option of disposal to rivers, sea or other watercourses has been used for many years, but with a greater awareness of environmental factors and stricter legislation governing the disposal of sludge, other sludge disposal methods are gaining popularity. One of the simplest and oldest methods is lagooning of sludges. When availability of land is not an issue and the climate is suitable, sludges can be effectively dried in lagoons. Lagoons offer an economic solution, although mechanical equipment is usually required eventually to remove the sludge build-up from the lagoons to nearby land or landfill sites (Water Quality and Treatment, 1990).

A disadvantage of lagoons is that some sludges, such as those formed when using aluminium sulphate for coagulation, do not dewater very well and also lagoons are fairly dependent on weather conditions. Higher disposal and labour costs are increasing the costs of lagooning and in many cases they are now comparable to the costs for mechanical dewatering and disposal.

Drying beds are another option for sludge disposal and these are used extensively in Southern Africa. Drying beds are an improvement on sludge lagoons as under-drains accelerate the drying process. However, the cost of removing the dried sludge can still be significant and may make mechanical dewatering systems more attractive (Water Quality and Treatment, 1990).

Gravity thickening of sludge can offer economic incentives, since the smaller volumes of sludge produced allow for smaller dewatering units, if these are to be used. Mechanical dewatering processes include linear screens, vacuum filtration, belt filters, filter presses and centrifuges (Water Quality and Treatment, 1990). All of these, including gravity thickening, are often assisted by the addition of small amounts of sludge treatment coagulants to the sludge.

Before the development of polyacrylamides, inorganic sludge coagulants were used. One of the most common, where feasible, was the use of quicklime (calcium oxide). Apart from its coagulating effect, it has the ability to remove hydrated water from the gelatinous aluminium hydroxide and ferric hydroxide sludges and thereby increase the solids content. The disadvantages of handling difficulties, scaling of equipment and the increased mass of sludge solids, have however greatly reduced its use and these days polyelectrolytes are almost invariably used.

Factors that influence the selection of a sludge-conditioning chemical are (Mortimer, 1991):

1. The nature of the sludge
2. The type of mechanical dewatering unit
3. The requirements on the dewatered sludge ‘cake’
4. The requirements on the clarity of the filtrate or centrate
5. The sludge solids content prior to dewatering.

The first four determine the type of sludge treatment polymer needed to treat the sludge in terms of chemical composition, molecular weight, charge density and type, while the sludge solids content influences the polymer dose

These sludge treatment coagulants have a low charge density and are generally anionic or non-ionic, since they are used to increase the floc size by bridging the existing flocs and not to satisfy the charge demand, which has usually been met during primary coagulation. These chemicals are also usually of a high molecular weight, since this assists in producing large flocs which can settle rapidly (Mortimer, 1991).

4.2 EVALUATION OF SLUDGE TREATMENT COAGULANTS

As with primary coagulants, sludge treatment coagulants are evaluated firstly in order to choose the most suitable product in terms of cost and performance for a particular application and secondly, having chosen the best product, to ensure that the quality remains consistent.

There are only a few tests available for the selection of sludge treatment methods and the same tests are used to monitor quality. Two of the tests described in this manual, measure the dewaterability of the sludge, which can be characterised by either the amount of moisture remaining in a sludge after dewatering or by the ease with which a sludge is dewatered (Chen *et al*, 1996). One of the most commonly used methods for determining the dewaterability or filterability of a sludge is to filter it through filter paper, or, in the case of a belt press, the actual belt press filter cloth, using a Buchner funnel and then measure the amount of filtrate collected over a designated period or measure the time taken to collect a given volume of filtrate (Baskerville and Gale, 1968; Chen *et al*, 1996).

The capillary suction time test provides a rapid and simple method of characterising the dewaterability of a sludge (Baskerville and Gale, 1968; Versilind, 1988). The time taken for the filtrate to travel a fixed distance through the filter paper is called the capillary suction time (CST), a short CST generally indicating good dewaterability and a long CST poor dewaterability (Chen *et al*, 1996). The CST test is however completely empirical (Versilind, 1988), meaning that it can only be used to compare polymeric coagulants on a single sample of sludge and cannot be used as an absolute value to compare the performance of coagulants on different sludge

samples or at different plants. In spite of this, CST provides a rapid and inexpensive means of evaluating different coagulants for use on plants in which mechanical dewatering units are used.

The third test is a simple settling test in which the volume of settled sludge after a prescribed period is measured. This test is useful for evaluating a sludge treatment coagulant in terms of its ability to improve the settling characteristics of the sludge. Experience has shown that the factors governing settling and dewatering are not always compatible and in many cases, a polymer that performs the best in terms of settleability, may not be the best in terms of dewaterability. This can be problematic in certain sludge treatment processes in which the sludge is thickened prior to being dewatered mechanically in a centrifuge, belt press etc. If facilities exist for only one sludge treatment coagulant, it is sometimes necessary to compromise when choosing a suitable coagulant, in order to find one that gives acceptable results both in the thickener and in the mechanical dewatering unit.

4.2.1 Recommended Procedure for Sludge Coagulant Selection.

When choosing a suitable product various manufacturers should be invited to submit samples for evaluation, but as with primary coagulants, it is recommended that each supplier be limited to between 1 and 3 products to prevent the assessment procedure from becoming too laborious.

The testing procedure used will depend on the treatment applications. For example, for a plant using mechanical dewatering units such as centrifuges and belt presses, the CST or filterability tests can be used, while for a process using gravity thickening, the settling test is better. For plants where both gravity thickening and mechanical dewatering processes exist, it is advisable to use the settling test as well as either the CST or filterability test. If facilities only exist for the storage and dosing of one sludge treatment coagulant, then it will be necessary to select a coagulant that gives acceptable performance in both tests.

It is important to use a representative sample of sludge and ensure that the solids content of the sludge falls within the usual operational range. It is not always possible to obtain a sludge sample of the correct solids content for CST and filtrability tests that does not already contain the sludge treatment coagulant being used on the plant, since if gravity settling precedes the mechanical dewatering unit, the sludge from the gravity thickener may already contain the polymer being used on the plant. In such

cases, it may be necessary to obtain a sample of sludge from the clarification process, thicken this sludge by settling, but retain any of the decanted supernatant, measure the solids content of the thickened sludge sample and then reconstitute it with supernatant to obtain a sludge sample of the desired solids content.

It is important in the case of the CST test that all tests be conducted on a single sample of sludge (i.e. collected at the same time), but it is also advisable to conduct the other tests on a single sample of sludge as well in order to obtain a better comparison of the different polymers. Dosages are measured in kg/tonne and can vary from below 1 kg/tonne to above 10 kg/tonne depending on the type of sludge and the solids content. If tests are being conducted on a plant for which historical data is available, then this can be used in determining the concentration range for the testing. If products are being evaluated for a new plant, selection of the correct dose range may be more difficult. Detailed descriptions of how to prepare solutions of sludge treatment coagulants, most of which are supplied in as granules or powders are given in Section 4.3.1 to 4.3.4 below and the method used to calculate the dose is also provided.

Once tests have been completed, the data should be collated and the best products in terms of both cost and performance selected, or if choosing a single product for both gravity thickening and mechanical dewatering applications, a product should be chosen that performs acceptably for both and is cost effective. Two to four of the most promising products should be selected and then full-scale plant trials conducted using each product. With sludge treatment coagulants, only a few hours are required to test a product on a mechanical dewatering unit, since retention times in these are short, but a longer period is required to test products on a gravity thickener. One should allow a period at least as long as four times the retention time of the gravity thickener in order to obtain a realistic indication of the performance of the product. In most cases a trial that lasts between one and two days is sufficient to test a product adequately on a gravity thickener.

4.2.2 Ensuring Consistent Product Quality.

Tests to ensure the consistency of quality of a sludge treatment coagulant once it has been selected, are not as simple as those used for primary coagulants. An apparent density test (Section 4.3.5) could provide some indication of changes in the quality of the product, but otherwise performance tests such as CST, filterability or settling tests carried out with the product being tested together with that of a retainer sample of the same product are the only reliable way of determining consistent in the quality of the chemical.

4.3 ANALYTICAL METHODS

4.3.1 SLUDGE DEWATERING PROCEDURE

1. Introduction

One of the ways of determining the filterability of sludge is to use a Buchner funnel and filter the sludge through a filter paper or alternatively a screen or a piece of the filter press screen being used on the plant, and to measure either the time taken to obtain a given volume of filtrate or the time it takes until the cake residue begins to crack. The larger the volume of filtrate collected in a given period or the shorter the time taken for the cake residue to crack, the better the filterability of the sludge.

2. Scope

This method may be used to determine the most effective product for sludge filterability for a belt press, by measuring a specific resistance of sludge under 0.5 bar vacuum. With this method the optimum doses of polymers may be determined, although it is necessary to take into account the compressibility factor.

3. Interferences

4. Hazards

5. Sample Collection

Samples may be collected in 25 L drums.

6. Apparatus

1. Pipettes
2. 500 mL capacity beakers
3. Measuring cylinder
4. Stirrer with variable speed control
5. Stop watch
6. Buchner funnel
7. Filter paper, screen or filter press cloth (cut to the size of the Buchner funnel)

7. Reagents

1. Polymers to be assessed.
2. 0,5% Polymers Solutions
    - Accurately weigh out 0,5g of the polymeric granules into a 150 mL glass beaker.
    - Place a magnetic stirrer bar into the granules and start to stir.
    - While stirring add 3 mL of methylated spirit, methanol or ethanol, in order to wet the granules.
    - Add 97 mL of distilled water and stir (the solution will be very viscous).
    - Solutions should be stored in the dark and discarded after 2 to 3 days.

8. Analytical Procedure

8.1 Selection of optimum mixing speed

1. Obtain a sludge sample to which no sludge treatment coagulant has been added.
2. Obtain the name and dosage of polymer presently being used to treat the sludge (if comparing performance to that on the plant).
3. Before removing an aliquot of sludge, mix the sample thoroughly.
4. Measure out a 200 mL aliquot into a 500 mL beaker.
5. Switch the stirrer to 600 rpm
6. Add the polymer dose which the plant is currently using to this sample
7. Stir for 15 seconds
8. Switch the stirrer off
9. Pour the treated sludge into the Buchner funnel, which contains the 600 µm mesh or the filter cloth.
10. Immediately start the stop watch.
11. Record the volume of filtrate at intervals of 3, 5, 10, 15, 20 and 30 seconds.
12. Also note the clarity and the fines present in the filtrate.
13. It may be necessary to increase the dose in order to get an acceptable result.
14. Repeat the test keeping the polymer dose constant and varying the stirrer speed (e.g. 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200 rpm).
15. The optimum speed will be the one that provides the highest volume of filtrate.
16. This has usually been found to be either 500 or 600 rpm for centrifuge applications and 200 rpm for belt press (low shear) applications.

8.2 Screening of new polymers

1. Establish the optimum mixing speed as described in **8.1** above.
2. Measure out a 200 mL aliquot into a 500 mL capacity beaker.
3. Switch the stirrer to optimum mixing speed.

4. Add the polymer dose required to this sample (suggested doses are 2, 4, 6, 8, 12 kg/ton)
5. Stir for 15 seconds.
6. Switch the stirrer off.
7. Pour 100 mL of the treated sludge into the Buchner funnel (final cake will be 8-10 mm thickness).
8. Turn on the vacuum and quickly achieve 0,5 bar (this must remain constant throughout the test).
9. Once the vacuum is attained, start the stopwatch and record the volume of filtrate already collected, volume V_0 corresponding to the time t= 0 that will have to be subtracted from the volumes collected later.
10. Record volumes of filtrate at intervals of 10, 15, 20, 30 or 60 seconds, according to the filtration rate.
11. Continue the test until the cake is dewatered (loss of vacuum due to the cracking of the cake).
12. This will be done for each sample of polymer

9. Calculations

Calculation for the specific resistance to filtration.

Volumes of filtrate V_0, V_1, V_2, V_3, etc. corresponding to the times T_0, T_1, T_2, T_3, etc. are recorded.

Record on a graph the points that have V_x as abscissa and the following as ordinate:

$$\frac{T_x}{v_x - v_o}$$

Theoretically, these points form a straight line (except at the beginning of filtration and during dewatering).

The slope of the linear portion of the curve obtained represents coefficient a.

The specific resistance under 0.5 bar (49×10^3 Pa) is given by the relationship:

$$r_{0.5} = \frac{2\, a\, PS^2}{\eta\, C}$$

a = coefficient in $s.m^{-6}$

P = head loss in Pascal (49×10^3)

S = surface area in m^2

η = dynamic viscosity of water: in Pa.s (at 20º C, near 1.1 x 10^{-3} Pa.s)

C = residue on evaporation at 105° C in $kg.m^{-3}$

r = specific resistance in $m.kg^{-1}$

NOTE: C, residual on evaporation at 105º C divided by the volume of sludge is an approximation of W (weight of suspended solids deposited per unit filtrate volume)

10. References

1. Supplied by Sud-Chemie, Business Unit Water Treatment, Floccotan.
2. "Water Treatment Handbook", 6th Ed., Degremont, Lavoisier Publishing, 1991.

4.3.2 ALTERNATIVE SLUDGE DEWATERING TEST PROCEDURE

1. Introduction

This test procedure is similar to that described in 4.3.1 above. Sludge is filtered through a mesh screen using a Buchner funnel for set periods of time. The optimum mixing speed and dosage are selected based on the conditions and coagulant that give rise to the highest volume of filtrate.

2. Scope

This method may be used to determine the most effective product for sludge dewatering applications, such as centrifuges, belt presses etc.

3. Interference

4. Hazards

5. Sample Collection

Samples may be collected in 25 L drums.

6. Apparatus

1. Pipettes
2. Square containers (90 X 110 mm) or 500 mL capacity beakers.
3. Measuring cylinder
4. Stirrer with variable speed control
5. Stop watch
6. Buchner funnel
7. 600µm Mesh screen (cut to the size of the Buchner funnel)
8. Square containers (90 X 110 mm) or 500 mL capacity beakers.

7. Reagents

1. Polymers to be assessed.
2. 0,5% Polymers Solutions
    - Accurately weigh out 0.5g of the polymeric granules into a 150 mL glass beaker.
    - Place a magnetic stirrer bar into the granules and start to stir.

- While stirring add 3 mL of methylated spirit, methanol or ethanol, in order to wet the granules.
- Add 97 mL of distilled water and stir (the solution will be very viscous).
- Solutions should be stored in the dark and discarded after 2 – 3 days.

8. Analytical Procedure

8.1 Selection of optimum mixing speed

1. Obtain a sludge sample to which no sludge treatment coagulant has been added.
2. Obtain the name and dosage of polymer presently being used to treat the sludge (if comparing performance to that on the plant).
3. Before removing an aliquot of sludge, mix the sample thoroughly.
4. Measure out a 200 mL aliquot into a square container or 500 mL capacity beaker.
5. Switch the stirrer to 600rpm.
6. Add the polymer dose which the plant is currently using, to this sample or select an appropriate dose based on experience.
7. Stir for 15 seconds.
8. Switch the stirrer off.
9. Pour the treated sludge into the Buchner funnel, which contains the 600 µm mesh.
10. Immediately start the stopwatch.
11. Record the volume of filtrate at intervals of 3, 5, 10,15, 20 and 30 seconds.
12. Also note the clarity and the fines present in the filtrate.
13. It may be necessary to increase the dose in order to get an acceptable result.
14. Repeat the test keeping the polymer dose constant and varying the stirrer speed (200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200 rpm).
15. The optimum speed will be the one that provides the highest volume of filtrate. This has been found to be either 500 or 600 rpm for centrifuge applications and 200 rpm for belt press (low shear) applications.

8.2 Screening of new polymers

1. Once the optimum mixing speed has been established, follow the same procedure as above keeping the mixing speed constant and vary the polymer dose (use doses such as 2,4,6, 8, 12 kg/ton).
2. This will be done for each sample of polymer.
3. The optimum dose is the one that provides the highest volume of filtrate.

9. Calculation

Based on the results of this test the best coagulant for a particular application and/or the optimum dose and treatment conditions (stirring speed) can be selected. Optimum products and conditions are determined from the amount of filtrate produced, more filtrate indicating better products and conditions. The clarity of the filtrate should also be used in the selection process.

10. References

1. Supplied by Sud-Chemie, Business Unit Water Treatment, Floccotan.

SLUDGE DEWATERING WORKSHEET 1

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

OBTAINING OPTIMUM DOSE			
Polymer name:	**Time sec**	**Volume of filtrate**	**Clarity/ fines present**
	3		
	5		
Current plant dose:	**10**		
	15		
	20		
	30		

Polymer dose remains constant vary stirrer speed								
200 rpm	**Volume**	**Clarity**	**300 rpm**	**Volume**	**Clarity**	**400 rpm**	**Volume**	**Clarity**
3 s			**3 s**			**3 s**		
5 s			**5 s**			**5 s**		
10 s			**10 s**			**10 s**		
15 s			**15 s**			**15 s**		
20 s			**20 s**			**20 s**		
30 s			**30 s**			**30 s**		
500rpm	**Volume**	**Clarity**	**600rpm**	**Volume**	**Clarity**	**700 rpm**	**Volume**	**Clarity**
3 s			**3 s**			**3 s**		
5 s			**5 s**			**5 s**		
10 s			**10 s**			**10 s**		
15 s			**15 s**			**15 s**		
20 s			**20 s**			**20 s**		
30 s			**30 s**			**30 s**		
800 rpm	**Volume**	**Clarity**	**900 rpm**	**Volume**	**Clarity**	**1000 rpm**	**Volume**	**Clarity**
3 s			**3 s**			**3 s**		
5 s			**5 s**			**5 s**		
10 s			**10 s**			**10 s**		
15 s			**15 s**			**15 s**		
20 s			**20 s**			**20 s**		
30 s			**30 s**			**30 s**		
1100rpm	**Volume**	**Clarity**	**1200rpm**	**Volume**	**Clarity**	**1300rpm**	**Volume**	**Clarity**
3 s			**3 s**			**3 s**		
5 s			**5 s**			**5 s**		
10 s			**10 s**			**10 s**		
15 s			**15 s**			**15 s**		
20 s			**20 s**			**20 s**		
30 s			**30 s**			**30 s**		

SLUDGE DEWATERING WORKSHEET 2

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

% SOLIDS				
Sample	**Mass 1**	**Mass 2**	**Mass 3**	**% Solids**
Average				

DOSE CALCULATIONS					
Dose	**Solids g/L**	**A**	**B**	**C**	**D**
2					
4					
6					
8					
12					

% solids X 10 = solids g/L

Where: A = 1000 000/ solids g/L
B = (dose/ A) x 1000
C = B/5
D = C/5 (for 0,5% poly) or C/1 (for 0,1% poly) = volume (mL) of poly to dose

SCREENING OF NEW POLYMERS					
Polymer	**Volume of filtrate per second**				
Kg/ton	**10**	**15**	**20**	**30**	**60**
2					
4					
6					
8					
12					

4.3.3 CAPILLARY SUCTION TIME (CST)

1. Introduction

The capillary suction time method is based on the principle that filtration of the sludge being tested is achieved by the suction applied to the sludge by the capillary action of a standard grade absorbent filter paper, such as those used for chromatography. A specially designed apparatus is used in which a standard size circular area in the middle of the absorbent paper is exposed to the sludge, while the rest of the paper is used to absorb the filtrate that is drawn out by the capillary suction of the paper. The time taken for the interface between the wet and dry portions of the paper to travel a given distance is measured electronically. The shorter the time taken, the better the filterability of the sludge will be.

2. Scope

This method may be used to determine filterability of water and wastewater sludge.

3. Interferences

Interferences are caused by the use of incorrect chromatography paper.

4. Hazards

5. Sample Collection

Samples may be collected in 25 L drums.

6. Apparatus

1. Pipettes
2. CST filter paper Rectangular Whatman no 17 with the rough side up.
3. CST apparatus

7. Reagents

1. Polymers to be assessed.
2. 0,5% Polymers Solutions
    - Accurately weigh out 0,5g of the polymeric granules into a 150 mL glass beaker.
    - Place a magnetic stirrer bar into the granules and start to stir.

- While stirring add 3 mL of methylated spirit, methanol or ethanol, in order to wet the granules.
- Add 97 mL of distilled water and stir (the solution will be very viscous).
- Solutions should be stored in the dark and discarded after 2 to 3 days.

8. Analytical Procedure

1. Use of the CST apparatus. See **FIGURE 4.1**.
2. Pipette 5 mL of treated sludge into the reservoir, resting on the filter paper.
3. Under the influence of the capillary suction of the paper, filtrate is drawn out of the sludge to saturate progressively a greater area of filtrate paper, causing the liquid front to advance outwards from the centre.
4. When the filtrate reaches the two probes 1A and 1B the increase in electrical conductivity between them causes the amplifier to start the clock. See **FIGURE 4.1**
5. When the filtrate reaches Probe 2, a change in conductivity between it and Probe 1A causes the clock to stop, registering the time interval.
6. For a given standard grade of paper, this time interval, CST, is quantitatively related to the filtration characteristics of the sludge.
7. The lower the CST the better the filterability of the sludge.

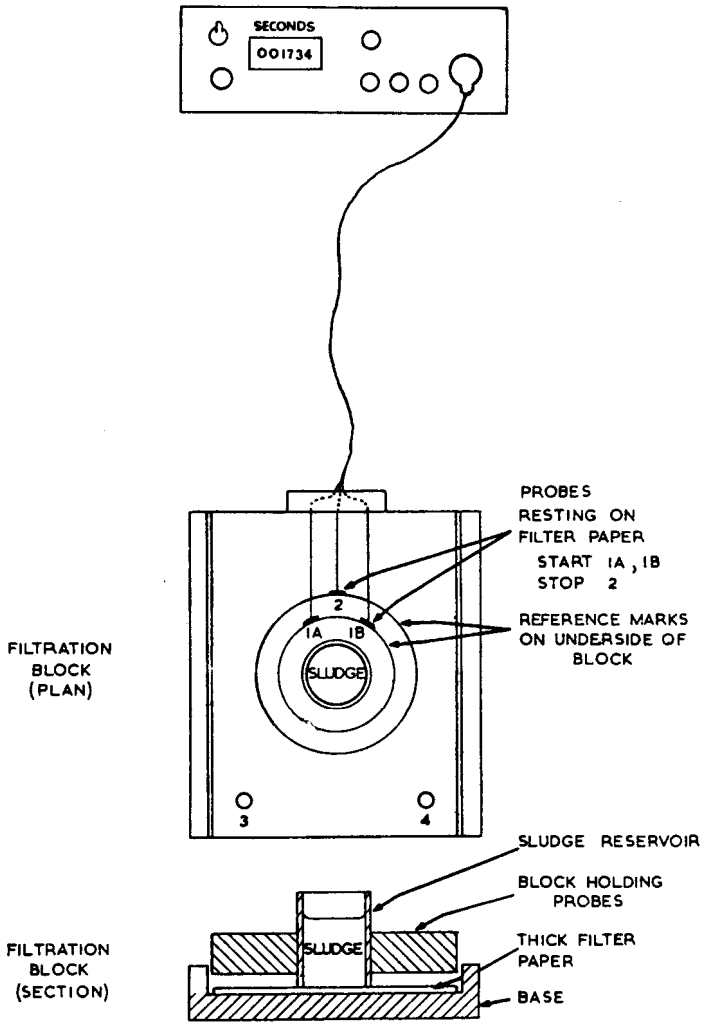


FIGURE 4.1: CST Apparatus.

9. Calculation

See attached work sheet for the calculations.

10. References

1. Baskerville, R.C.; and Gale,R.S.; “A Simple Automatic Instrument for Determining the Filterability of Sewage Sludges”, *Journal of the Institute of Water Pollution Control* No 2, pp 3 – 11, 1968.

CAPILLARY SUCTION TIME WORKSHEET 1

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

% SOLIDS				
Sample	**Mass 1**	**Mass 2**	**Mass 3**	**% Solids**
Average				

DOSE CALCULATIONS					
Dose	**Solids g/L**	**A**	**B**	**C**	**D**
2					
4					
6					
8					
12					

% solids X 10 = solids g/L

Where: A = 1000 000/ solids g/L

B = (dose/ A) x 1000

C = B/5

D = C/5 (for 0,5% poly) or C/1 (for 0,1% poly) = volume (mL) of poly to dose

CAPILLARY SUCTION TIME WORKSHEET 2

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

SCREENING OF NEW POLYMERS			
Polymer name:			
Polymer kg/ton	**Time in seconds**		
	10	**30**	**60**
2			
4			
6			
8			
10			
Polymer name:			
Polymer kg/ton	**Time in seconds**		
	10	**30**	**60**
2			
4			
6			
8			
10			

4.3.4 SETTLEABILITY TEST

1. Introduction

Sludge treatment often involves only settling of the sludge. Even when dewatering processes are used, the sludge is often gravity thickened prior to treatment in a centrifuge, belt press or other dewatering process. In such cases, selection of the best coagulant and optimum treatment conditions should be based on tests that assess settling of the sludge as opposed to the dewaterability of the sludge.

2. Scope

This method may be used to determine the settleability of water and wastewater sludge.

3. Interferences

4. Hazards

5. Sample Collection

Samples may be collected in 25 L drums.

6. Apparatus

1. Pipettes
2. Beakers
3. Measuring cylinder
4. Stirrer with variable speed control
5. Stop watch

7. Reagents

1. Polymers to be assessed.
2. 0,5% Polymers Solutions
    - Accurately weigh out 0,5 g of the polymeric granules into a 150 mL glass beaker.
    - Place a magnetic stirrer bar into the granules and start to stir.
    - While stirring add 3 mL of methylated spirit, methanol or ethanol, in order to wet the granules.
    - Add 97 mL of distilled water and stir (the solution will be very viscous).

- Solutions should be stored in the dark and discarded after 2 to 3 days.

8. Analytical Procedure

8.1 Selection of optimum mixing speed

1. Obtain a sludge sample to which no sludge treatment coagulant has been added.
2. Obtain the name and dosage of polymer presently being used to treat the sludge (if comparing performance to that on the plant).
3. Before removing an aliquot of sludge, mix the sample thoroughly.
4. Measure out a suitable volume of sludge (500 mL or 1 L, but other volumes can be used) into a beaker or square container of suitable capacity.
5. Switch the stirrer to 600 rpm.
6. Add the polymer being used on the plant at the dose currently being used.
7. Stir for 15 seconds.
8. Switch the stirrer off.
9. Pour the treated sludge into a measuring cylinder of adequate capacity.
10. Immediately start the stopwatch.
11. Record the volume of settled sludge at 15 minutes and 30 minutes.
12. Note the clarity of the filtrate.
13. It may be necessary to increase the dose in order to get an acceptable result.
14. Repeat the test keeping the polymer dose constant and varying the stirrer speed (200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200 rpm).
15. The optimum speed will be the one that provides the smallest volume of settled sludge after settling and the best quality filtrate.

8.2 Screening of new polymers

1. Once the optimum mixing speed has been established, follow the same procedure as above keeping the mixing speed constant and vary the polymer dose (use doses such as 2, 4, 6, 8, 12 kg/ton).
2. This will be done for each sample of polymer.
3. The optimum dose is again the one that provides the smallest volume of settled sludge with the best clarity.

9. Calculation

The optimum coagulant, coagulant dose and treatment conditions are selected based on the product and conditions that give the smallest volume of settled sludge and best clarity filtrate.

10. References

1. Process Services, Umgeni Water.

SETTLEABILITY TEST WORKSHEET 1

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

% SOLIDS				
Sample	**Mass 1**	**Mass 2**	**Mass 3**	**% Solids**
Average				

DOSE CALCULATIONS					
Dose	**Solids g/L**	**A**	**B**	**C**	**D**
2					
4					
6					
8					
12					

% solids x 10 = solids g/L

Where: A = 1000 000/ solids g/L

B = (dose/ A) x 1000

C = B/5

D = C/5 (for 0,5% poly) or C/1 (for 0,1% poly) = volume (mL) of poly to dose

OPTIMUM MIXING SPEED			
Mixing speed rpm	**15 minutes**	**30 minutes**	**Clarity**
Control 600			
200			
300			
400			
500			
600			
700			
800			
900			
1000			
1100			
1200			

SETTLEABILITY TEST WORKSHEET 2

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

SCREENING NEW POLYMERS			
Name of Polymer:			
Optimum mixing speed: rpm			
Kg/ton	**15 minutes**	**30 minutes**	**Clarity**
2			
4			
6			
8			
12			

SCREENING NEW POLYMERS			
Name of Polymer:			
Optimum mixing speed: rpm			
Kg/ton	**15 minutes**	**30 minutes**	**Clarity**
2			
4			
6			
8			
12			

SCREENING NEW POLYMERS			
Name of Polymer:			
Optimum mixing speed: rpm			
Kg/ton	**15 minutes**	**30 minutes**	**Clarity**
2			
4			
6			
8			
12			

4.3.5 APPARENT DENSITY OF POLYACRYLAMIDE POWDER OR GRANULES

1. Introduction

The apparent density of polyacrylamide powder or granules can be used as a quality control parameter. The mass of a measured volume of settled solid polyacrylamide powder or granules can be used to determine an apparent density.

2. Scope

This method may be used to determine the apparent density of polyacrylamide powder or granules.

3. Interferences

4. Hazards

5. Sample Collection

Samples of polyacrylamide may be collected in 500 mL containers.

6. Apparatus

1. Graduated beakers
2. Electronic balance capable of weighing to four decimal points of a gram.

7. Reagents

1. Polymers to be assessed.

8. Analytical Procedure

1. Place approximately 50 mL (other volumes can be used which are suitable for the mass range of the balance) into a 100 mL (or suitable size) pre-weighed beaker and weigh contents and beaker.
2. Tap the beaker until no more settling of the polyacrylamide occurs.
3. Record the volume occupied by the settled polyacrylamide.

9. Calculation

The apparent density is determined using the following:

$$\frac{M2 - M1}{V}$$

Where:

M1 = Mass of beaker

M2 = Mass of beaker and polyacrylamide

V = Settled volume of polyacrylamide

10. References

1. Process Services, Umgeni Water.

POLYACRYLAMIDE WORKSHEET

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

BULK DENSITY			
Sample	**M1**	**M2**	**Bulk density kg/m^3**

5. pH ADJUSTMENT AND STABILISATION CHEMICALS

5.1. INTRODUCTION

Chemicals such as lime, soda ash, sodium bicarbonate and sodium hydroxide are used widely in water and wastewater treatment for a variety of different applications, including pH correction, stabilisation and lime softening. The pH of a water is very important in water treatment for a number of reasons. pH affects many of the chemical reactions which occur in the water, such as the reaction of an inorganic coagulant. For example, when using aluminium sulphate, the optimum pH for turbidity removal is around 6,8, while precipitation of the organic matter present is best at a pH of around 5. However, the addition of aluminium sulphate results in a reduction in the pH, since for every 1 mg/L of aluminium sulphate that reacts to produce a precipitate of aluminium hydroxide, 0,5 mg/L of alkalinity (as $CaCO_3$) is consumed (Water Quality and Treatment, 1990). This reduction in the alkalinity and subsequently the pH may necessitate the addition of lime or soda ash in order to raise the pH to a value that is ideal for a particular application. Inorganic coagulants are often used in wastewater treatment for applications such as phosphate removal, and here too reductions in the pH of the sewage occur depending on the alkalinity content. If the reduced alkalinity is not replaced, the microbes essential for the process will be affected and may even die.

The pH is also important in disinfection reactions. Taking the common example of chlorine or hypochlorite disinfection, the pH affects the proportion in which the various species of chlorine occur. At a pH of around 6,5, HOCl predominates, while at a pH of 9, OCl^- is the predominant species (White, 1992). This has very important implications because HOCl is a much more powerful disinfectant than OCl^-. Adjusting the pH to the correct value allows for better disinfection and more cost effective utilisation of the chlorine.

One of the most important applications for lime, soda ash and sodium bicarbonate is in stabilisation of soft waters or softening of hard waters. Soft waters are low in

alkalinity and are therefore corrosive. All waters are corrosive to some extent, but the corrosion due to soft waters can substantially increase water treatment costs due to deterioration in pipes and pumps, which can lead costly repairs, water losses due to leaks in the pipes and drops in water pressure. Leaching due to corrosion can also result in increased concentrations of metals in the potable water supply and with certain pipe materials, toxic metals such as lead and cadmium can be released into the water. Cement pipes are also very susceptible to corrosion in low alkalinity water. Other problems caused by corrosion include bad tastes, odours and bacterial slimes, which in turn can deplete disinfectant residuals in the water (Water Quality and Treatment, 1990). Adjustment of the pH is the most commonly used method of reducing corrosion and although it does not always eliminate corrosion completely, it can significantly diminish the problem.

Hard waters cause scaling of pipes and eventual blockage of the pipe. Chemical precipitation using lime, lime-soda ash or caustic soda can be used to soften the water and is usually used in rapid-mix, flocculation and sedimentation process trains like those typically found in conventional water treatment plants, although a solids-contact softener which combines these processes into one unit, can also be used. The selection of chemical depends on a number of factors, including cost, total dissolved solids content, the carbonate and non-carbonate hardness and the chemical stability of the water. For example, water that contains little or no non-carbonate hardness can be softened using only lime, but for waters high in non-carbonate hardness, it may be necessary to use both lime and soda ash to reduce the hardness sufficiently (Water Quality and Treatment, 1990; Sanks, 1978). Once a water has been softened, it has high causticity and scale-formation potential and therefore needs to be recarbonated in order to reduce the pH and alleviate scaling in the downstream pipelines (Water Quality and Treatment, 1990).

Lime or lime-soda ash softening tend to be more cost effective than caustic softening, they often result in a decrease in the total dissolved solids content of the water and produce more sludge than the caustic softening process. Caustic soda has the advantage of not deteriorating as rapidly during storage, whereas slaked lime can absorb carbon dioxide and water during storage and quick lime may react with moisture and undergo slaking, resulting in feeding problems (Water Quality and Treatment, 1990).

5.2. EVALUATION OF pH AND STABILISATION CHEMICALS

5.2.1. Lime

Lime is mined as limestone ($CaCO_3$) and then heated in kilns to produce quicklime (CaO). It can then be slaked or hydrated to produce slaked/hydrated lime ($Ca(OH)_2$). It is in the form of quicklime or slaked lime that lime is most commonly used in water and wastewater treatment applications. Quicklime has a number of advantages over slaked lime, these being (Water Treatment Handbook, 1991):

- Lower costs
- A higher CaO content
- A higher bulk density (0,7 to 1,1, compared to 0,3 to 0,6 for slaked lime)

However, if using quicklime, it is necessary to have facilities for slaking the lime, which increases the capital investment. Another disadvantage is that the quality of quicklime tends to be more variable than that of slaked lime.

Lime is often used in very large quantities and in such cases, it is usually purchased as quicklime and then slaked in conjunction with the feeding process. It can be purchased as pebble lime to reduce the problems due to dusting, or in a powder form if using lime from recalcining calcium carbonate sludge. Hydrated lime is generally purchased in powder form and then a slurry is produced for dosing purposes (Sanks, 1978).

As mentioned in the Introduction, if not properly stored, quicklime may slake and slaked lime may absorb carbon dioxide and water from the air to form $CaCO_3$ (Water Quality and Treatment, 1990).

It is important when using lime that it contains the correct amount of active ingredient is of a suitable quality, so as to avoid operational problems and that it does not contain contaminants in concentrations high enough to cause either health related problems or affect the treated water aesthetically. The specifications for the various types and grades of quicklime and hydrated (slaked) lime can be found in SABS 459-1955 Standard Specification for Lime for Chemical and Metallurgical Purposes, together with analytical procedures for measuring these. However, many of these procedures are time consuming, gravimetric procedures and faster, easier procedures are available in some cases. When selecting lime, measurement of the

concentration of the lime is important. For both quicklime and hydrated lime, the "available" calcium oxide content gives an indication of the purity of the lime. In the case of quicklime, the "available" calcium oxide content should be at least 90% for Type I quicklime as specified in SABS 459-1955, while the minimum "available" calcium oxide content of Grade I hydrated lime is 68% according to the same standard. Converting a calcium oxide content of 68% in hydrated lime to its equivalent calcium hydroxide content yields a calcium hydroxide content of 90% (i.e. $^{68\%}/_{56}$ x 74), in other words the same level of purity as that for quicklime. A titration procedure for the measurement of the calcium oxide content can be used to determine the purity of both quicklime and hydrated lime, although in the case of hydrated lime, one also needs to ensure that adequate conversion of calcium oxide to calcium hydroxide has occurred. An available lime content test can be conducted for this purpose and should yield a minimum of 68% when reported as CaO and 90% when reported as $Ca(OH)_2$.

The grit content or sieve analysis of a lime is important in terms of process operation. High grit content can cause mechanical problems with pumps and feed impellers and in order to prevent damage to equipment, the grit content should not exceed 5% (SABS 459-1955). This is determined by measuring the residue retained on a 150 µm sieve.

Tests for other contaminants such as silica and insoluble mineral matter can also be used to assess the quality of the lime, but usually measurement of the available CaO and $Ca(OH)_2$ concentrations and the grit content of a lime is adequate for this purpose. Determination of the carbon dioxide content of hydrated lime will reveal whether deterioration of the lime is occurring during storage.

5.2.2. SODIUM HYDROXIDE

Sodium hydroxide, commonly known as caustic soda, is supplied in a variety of forms; it is available in flakes, lumps or powder as 98,9% NaOH. Solid sodium hydroxide is highly hygroscopic, readily absorbing moisture from the air, which can make storage of this product in humid atmospheres problematic. In addition, it is dangerous to handle and can result in serious alkaline burns to the skin and eyes. It dissolves very readily, solubility increasing significantly as the temperature increases,

with large amounts of heat being generated during dissolution. It is therefore often preferable to purchase sodium hydroxide in liquid form as a 50% NaOH solution, which begins to crystallise at temperatures of 12°C (Sanks, 1978).

It is important to ensure that the hydroxide content of the caustic soda is within the range specified by the supplier. A simple acid base titration procedure that is described in Section 5.3.5, can be used for this purpose. Sodium hydroxide solution deteriorates only very slowly during storage.

5.2.3. SODA ASH (SODIUM CARBONATE)

The chemical formula for soda ash is Na_2CO_3 and it is available as dense granules, medium granules and powder and as light powder. Dense soda ash contains a water of crystallisation (Na_2CO_3/H_2O), while light soda ash does not (Na_2CO_3) and in most cases dense soda ash is used, as it is more economical to ship and transport. Soda ash is very soluble (12,5% at 10°C) and is not corrosive, but bulk-handling equipment should include dust collection equipment (Sanks, 1978).

Soda ash is suitable for small plant applications, since it is easier to handle and dose than lime. It is also ideal for post-filter pH stabilisation of alum treated water. Lime must be used prior to the filters, otherwise it will result in an increase in turbidity, but soda ash can be used after the filters and because of its high solubility, it will not affect the turbidity of the water. Soda ash is also used for pH stabilisation of very low alkalinity waters, since the formation of insoluble carbonates, which protect against corrosion, occurs when using this chemical (Water Quality and Treatment, 1990).

5.2.4. SODIUM BICARBONATE

Sodium bicarbonate (Na_2HCO_3) is readily soluble and easy to handle and like soda ash is used for pH stabilisation of low alkalinity waters (Water Quality and Treatment, 1990).

5.3. ANALYTICAL METHODS

5.3.1. CALCIUM OXIDE CONTENT OF LIME

1. Introduction

The calcium oxide concentration gives an indication of the purity of the lime. In the case of quicklime, the calcium oxide content should be at least 90% for Type I quicklime as specified in SABS 459-1955, while the minimum calcium oxide content of Grade I hydrated lime is 68% according to the same standard. Converting a calcium oxide content of 68% in hydrated lime to its equivalent calcium hydroxide content yields a calcium hydroxide content of 90% (i.e. $^{68\%}/_{56}$ x 74), in other words the same level of purity as that for quicklime. A titration procedure for the measurement of the calcium oxide content can be used to determine the purity of both quicklime and hydrated lime

2. Scope

This method may be used to determine the calcium oxide content of lime samples.

3. Interferences

4. Hazards

Sodium hydroxide. Ensure that you are familiar with the dangers and treatment associated with the above substance.

5. Sample Collection

Samples may be collected in either glass or plastic containers.

6. Apparatus

1. Burette digital or glass
2. Volumetric equipment
3. A-grade glassware

7. Reagents

Use only distilled water.

All prepared solutions are made up in volumetric flasks and are stored in glass containers, unless otherwise indicated.

1. Sodium Hydroxide Buffer solution
    - Dissolve 100 g NaOH in 500 mL distilled water. Allow to cool. Store solution in a plastic bottle.
2. Triethanolamine Solution 30% V/V
    - Dilute 3 volumes of triethanolamine with 7 volumes of distilled water and mix until the solution is homogenous.
    - Only mix sufficient quantities for immediate use.
3. Cal-Red indicator
    - 0,5g P+R reagent (2-hydroxy-1-(2Hydroxy-4-sulpho-1-Napthyl LA 20)-3-Napthoil Acid) is mixed with 50 g sodium chloride in a porcelain mortar.
4. EDTA
    - Dissolve 50 g of EDTA salt in distilled water and dilute to 5 litres.
    - Allow to stand overnight before using.
5. Calcium Standard solution
    - Purchase Riedel-de-Haën Calcium standard 1,00 g Calcium or similar as the chloride, water soluble (commonly known as a Fixanol solution).

8. Analytical Procedure

8.1 Calculation of CaO Factor

1. Pipette 50 mL of standard Ca solution into a 300 mL conical flask.
2. Add 50 mL of hot distilled water.
3. Add 10 mL of a 30% Triethanolamine solution
4. Add 5 mL NaOH buffer solution
5. Add 0,2 g solid Cal-Red indicator
6. Titrate against EDTA
7. Colour changes from wine-red through purple to sky blue.
8. Take end point at purple to sky-blue changeover. Record Titre (CaO) in mL.

$$\text{CaO factor} = \frac{34{,}98}{\text{Titre (CaO) mL}}$$

8.2 Calculation of Sample CaO

1. Accurately weigh out 1,00 g of the lime sample and record mass.
2. Transfer to a beaker and add 30 mL distilled water and 5 mL of concentrated hydrochloric acid.
3. Cover the beaker and boil gently for 5 minutes
4. Cool the solution
5. Transfer to a 500 mL volumetric flask
6. Make up to the mark and shake well
7. Pipette 50 mL aliquot of this solution into a 300 mL conical flask
8. Proceed as for standard solution.

9. Calculation

$$\% \text{ CaO} = (\text{CaO Factor}) \text{ X } (\text{Sample CaO Titre})$$

10. References

1. Sappi Saicor Methods Manual.
2. South African Bureau of Standards 459-1955 Standard Specification of Lime for Chemical and Metallurgical purposes.

5.3.2. ALTERNATIVE METHOD FOR CALCIUM OXIDE

1. Introduction

The calcium oxide concentration of a lime sample (quicklime or hydrated lime) is an important indicator of the purity of the lime. The SABS 459-1955 specifies that the calcium oxide content of Type I quicklime should be at least 90% and that for Grade 1 hydrated lime should be 68%. The method described in this procedure provides a rapid method for determination of the calcium oxide content of quicklime and hydrated lime. It measures total base and expresses this as calcium. It is therefore not accurate for dolomitic (high magnesium) limes.

2. Scope

This method describes a shortened procedure for the determination of the calcium oxide content in lime.

3. Interferences

4. Hazards

Dust: ensure you are familiar with the dangers and treatment associated with dust.

5. Sample Collection

Samples may be collected in either plastic or glass containers or packets.

6. Apparatus

1. 50 mL Burette
2. 250 mL Erlenmeyer flasks
3. Analytical balance
4. A grade glass pipettes
5. 1 L glass Schott bottles or equivalent for shaking.
6. Mechanical shaker
7. Buchner filter and vacuum pump
8. Whatman No 42 filter papers

7. Reagents

1. Hydrochloric acid 0,1 N
    - Add approximately 8,9 mL of hydrochloric acid to 1 litre of distilled water.
2. Sucrose
3. Phenolphthalein indicator

8. Analytical Procedure

1. Accurately weigh 1,00 g of lime into a beaker, record mass.
2. Transfer to a 250 mL conical flask that contains 50 mL of distilled water.
3. Add 10 g of sucrose, stopper the flask and shake vigorously for 12 to 15 minutes on the shaker.
4. Filter through a Buchner filter using a vacuum pump and two no 42 Whatman filter papers.
5. Wash the flask with 6 separate 25 mL portions of cold distilled water and titrate against 0,1 N HCL using phenolphthalein as indicator.
6. Standardization of 0,1 N HCL
    - Accurately weigh 0,15 g of anhydrous sodium carbonate (previously heated to 260º C for 2 hours and cooled in a desiccator) into a 250 mL conical flask and dissolve in 25 mL of distilled water.
    - Titrate with 0,1 N HCL solution using screened methyl orange as indicator. The colour change is green to grey to violet endpoint.

9. Calculations

$$\text{N HCL} = \frac{1000 \times \text{mass } Na_2CO_3 \text{ (g)}}{53 \times \text{Av. titre (mL)}}$$

$$\% \text{ CaO} = \frac{\text{Titration (mL)} \times 0{,}02835}{\text{sample mass (g)} \times 100}$$

$$\% \text{ } Ca(OH)_2 = \text{CaO} \times 1{,}3213$$

10. References

1. Nelson Mandela Metropolitan Municipality, Scientific Services Division.
2. South African Bureau of Standards 459-1955 Standard Specification of Lime for Chemical and Metallurgical purposes.

5.3.3. AVAILABLE LIME (HYDRATED LIME)

1. Introduction

When quicklime is slaked to produce slaked or hydrated lime, calcium oxide is converted to calcium hydroxide. Determination of the calcium oxide content gives an indication of the purity of the hydrated lime, but gives no indication of the conversion to calcium hydroxide that occurred during slaking. It is important to ensure that the lime has been properly slaked before using it for treatment applications. This method is also not suitable for dolomitic lime, except as an approximation.

2. Scope

This method describes a procedure for the determination of available lime content of hydrated lime.

3. Interferences

4. Hazards

Dust: ensure you are familiar with the dangers and treatment associated with dust.

5. Sample Collection and Preservation

Samples may be collected in either plastic or glass containers or packets.

6. Apparatus

1. 50 mL Burette
2. 250 mL Erlenmeyer flasks
3. Analytical balance
4. A grade glass pipettes
5. 1 L glass Schott bottles or equivalent for shaking.
6. Mechanical shaker

7. Reagents

1. Hydrochloric acid 0,1 N
   - Add approximately 8,9 mL of hydrochloric acid to 1 litre of distilled water.
2. Screened methyl orange indicator.
   - Dissolve 0,5 g of methyl orange and 0,7 g of xylene cyanole red FF in 250 mL of 50% ethyl alcohol.
3. Phenolphthalein indicator
4. Sugar solution 7,5%
   - Prepare a 7,5% solution (75 g/L) of white cane sugar in distilled water and approximately 2 to 3 mL of supernatant from lime solution, having allowed this solution to stand, until the sugar solution is slightly alkaline to phenolphthalein.

8. Analytical Procedure

1. Accurately weigh 2,00 g of lime into a beaker, record mass.
2. Transfer to a 1 litre bottle and add 1000 mL of the sugar solution, tighten lid.
3. Agitate continuously for 4 hours on a shaker.
4. Remove the bottle and allow to settle for 10 to 15 hours.
5. Transfer 50,0 mL of the supernatant into a 250 mL Erlenmeyer flask.
6. Immediately titrate with standard 0,1 N hydrochloric acid using phenolphthalein as indicator.
7. Blank
   - Make a blank determination following the same procedure, using the same amounts of reagents. Subtract the blank titration from the millilitres titrated in the determination.
8. Standardization of 0,1 N HCL
   - Accurately weigh 0,15 g of anhydrous sodium carbonate (previously heated to 260º C for 2 hours and cooled in a desiccator) into a 250 mL conical flask and dissolve in 25 mL of distilled water.
   - Titrate with 0,1 N HCL solution using screened methyl orange as indicator. The colour change is green to grey to violet endpoint.

9. Calculation

$$\text{N HCL} = \frac{1000 \times \text{mass } Na_2CO_3 \text{ (g)}}{53 \times \text{Av. titre (mL)}}$$

$$\text{Available lime \%} = \frac{a \times N \times 56{,}08}{B}$$

Where:

a = volume of standard HCl used in the titration, after deduction of blank in mL.

N = normality of HCl.

B = weight of sample taken in g.

10. References

1. South African Bureau of Standards 459-1955 Standard Specification of Lime for Chemical and Metallurgical purposes.

5.3.4. SIEVE GRADING FOR LIME

1. Introduction

The presence of inorganic matter or grit in lime can cause operational problems, damaging pumps and feed impellers. Therefore, in order to prevent equipment from being damaged in this way, the grit content of a lime should not exceed a maximum of 5% according to the SABS 450-1955 Specification for Lime for Chemical and Metallurgical Purposes. This is determined by measuring the residue retained on a 150 µm sieve.

2. Scope

This method describes a procedure for the determination of the percentage grit content in brown or white lime.

3. Interferences

4. Hazards

Dust: ensure you are familiar with the dangers and treatment associated with each of the above substance

5. Sample Collection and Preservation

Samples may be collected in either plastic or glass containers or packets.

6. Apparatus

1. Analytical balance.
2. Evaporating dish or metal crucible.
3. Sieve of pore size 149 µm or A.S.T.M. No.100

7. Reagents

None

8. Analytical Procedure

1. Record the mass of the empty crucible or evaporating dish.
2. Weigh out 200.0g of hydrated lime into the sieve and brush through with a fine stream of water.
3. Continue washing until the water coming through the sieve is clear.
4. Transfer the residue retained on the sieve to a metal crucible or evaporating dish and dry at 100 to 120º C to a constant mass. Record the mass of the residue.

Sources of Error

Ensure that the water pressure is not too high as to splash some of the suspension out of the sieve.

9. Calculation of Results

$$\% \text{ Grit} = \frac{(M1 - M2) \times 100}{200}$$

Where:

M1 = mass of empty dry crucible or dish (g).

M2 = mass of crucible or dish plus dry residue (g).

10. References

1. South African Bureau of Standards 459-1955 Standard Specification of Lime for Chemical and Metallurgical purposes.

LIME QUALITY CONTROL

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

STANDARDISATION OF HCl			
Sample	**Mass $CaCO_3$**	**HCl (mL)**	**N HCl**
Titre 1			
Titre 1			
Average			

DETERMINATION OF CaO FACTOR		
Sample	**mL EDTA**	**Factor**
Titre 1		
Titre 1		
Average		

CALCIUM OXIDE			
Sample	**Mass of lime (g)**	**mL EDTA**	**% CaO**
Blank			
Titre 1			
Titre 2			
Average			

AVAILABLE LIME			
Sample	**Mass of lime (g)**	**mL HCl**	**% Lime**
Blank			
Titre 1			
Titre 2			
Average			

% GRIT		
Mass 1	**Mass 2**	**% Grit**

5.3.5. DETERMINATION OF ALKALINITY

1. Introduction

Alkalinity is a measure of the ability of a water to neutralise acids. Alkalinity consists of dissolved alkalis (monovalent oxides such as sodium and potassium) and alkaline earths (divalent oxides such as calcium and magnesium).

2. Scope

This method may be used to determine the total alkali content of bulk sodium carbonate, sodium bicarbonate, or sodium hydroxide.

3. Interferences

4. Hazards

Hydrochloric acid: ensure that you are familiar with the dangers and treatment associated with each of the above substances.

5. Sample Collection

Samples may be collected in either bags or plastic containers.

6. Apparatus

1. Burette
2. Volumetric equipment.
3. A-grade glassware.

7. Reagents

Use only distilled water.

All prepared solutions are made up in volumetric flasks and are stored in glass containers, unless otherwise indicated.

1. Sodium carbonate (anhydrous AR grade).
2. 0,1 N Hydrochloric acid
    - Add 8,9 mL of hydrochloric acid to a 1 L volumetric flask and make to the mark using distilled water.
3. Phenolphthalein

- Dissolve 0,5 g of phenolphthalein in 50 mL of methanol or ethanol, then dilute to 100 mL with water. Filter if necessary.

4. Methyl orange indicator
   - Prepare a 0,2% solution of methyl orange in 50% alcohol.
   - Colour change: yellow – orange – red.
5. Screened methyl orange indicator
   - Mix equal volumes of a 0,2% solution of methyl orange and 0,3% solution of xylene cyanol FF. Both are prepared in 50% alcohol.
   - Colour change: green – grey – red.

8. Analytical Procedure

1. Standardization of 0,1 N HCl.
   - Accurately weigh 1,325 g of anhydrous sodium carbonate (AR grade previously heated to 260º C for 2 hours and cooled in a desiccator) into a 250 mL volumetric flask. Dissolve in distilled water and then dilute to the mark.
   - Actual normality of the standard sodium carbonate solution can be calculated as follow:

$$N_1 = \frac{\text{mass } Na_2CO_3 \text{ x } 4}{53}$$

   - Titrate 25 mL portions of this solution with 0,1 N HCL solution using screened methyl orange as indicator. The colour change is green to grey to violet endpoint.
   - The concentration of the HCl solution can be calculated as follows:

$$\text{N HCl} = \frac{25 \text{ x } N_1}{\text{volume HCl (mL)}}$$

2. If testing sodium carbonate, weigh out approximately 2 g of anhydrous material or 5 g of the decahydrate and record mass accurately.
3. If testing sodium bicarbonate, weight out approximately 3 g of material and record mass accurately.
4. If testing sodium hydroxide, weigh approximately 10 g of solution (50% or proportionately more for lower concentrations) and record mass accurately.
5. Transfer to a 250 mL conical flask containing approximately 50 mL of distilled water.
6. Add 4 drops of phenolphthalein indicator.

7. Titrate against 0,1 N HCl to the first disappearance of the pink colour. Record this volume as Vp.
8. To the same flask, now add 4 drops of methyl orange or screened methyl orange indicator and titrate to the end point colour of the indicator. Record this volume as Vm.

9. Calculation

Calculation of phenolphthalein (hydroxide) alkalinity:

$$\% \text{ P Alkalinity as NaOH} = \frac{\text{Vp (ml) x N HCl x 40}}{\text{10 x mass (g)}}$$

$$\% \text{ M Alkalinity as } Na_2CO_3 = \frac{\text{Vm x N HCl x 53}}{\text{10 x mass (g)}}$$

$$\% \text{ Total Alkalinity as } Na_2CO_3 = \frac{\text{(Vp + Vm) x N HCl x 53}}{\text{10 x mass (g)}}$$

10. References

1. British standard specification for sodium carbonate. B.S. 3674:1963
2. British standard for Photography – Processing Chemicals - Specifications for sodium hydroxide. B.S. ISO 3617:1994.
3. “Standard Methods for the Examination of Water and Wastewater”, 20th Edition, Edited by L. S. Cleseceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.

ALKALINITY

Sodium carbonate/ sodium hydroxide

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

STANDARDISATION OF HCl			
Sample	**Mass $CaCO_3$**	**HCl (mL)**	**N HCl**
Titre 1			
Titre 1			
Average			

ALKALINITY						
Sample	**Mass (g)**	**V_p**	**V_m**	**% P Alkalinity**	**% M Alkalinity**	**Total Alkalinity**

6. OXIDANTS AND DISINFECTANTS

6.1. INTRODUCTION

The processes of oxidation and disinfection in water treatment are often inter-connected in that many of the chemicals used for both processes are the same. Most disinfectants are also strong oxidants and the effect of the chemical depends on the stage in the process at which it is added. Although the two processes cannot be completely separated, oxidation processes tend to predominate if the chemical is added early in the process (e.g. before coagulation), while disinfection processes generally take place when the chemical is added after treatment is essentially complete (i.e. after filtration).

This chapter deals with the removal of taste and odours, pre-oxidation, and disinfection, and the chemicals used for these processes and the tests employed to measure and monitor them.

6.2. TASTE AND ODOUR REMOVAL

Taste or odours in water may be due to the nature of the water, the suspended material, dissolved organics or breakdown products from organic matter such as vegetation or pollution, or compounds released by algae present in the water.

A variety of processes are used for removing taste and odours in the potable water treatment process. The method of removal depends on the nature of the taste itself. For example, the mineral composition of the water can be responsible for imparting a certain taste to the water and this is not easily addressed. Other tastes may be present due to volatile compounds such as hydrogen sulphide or volatile organic compounds (VOCs) such as toluene or ethylbenzene. The removal of such tastes is often carried out by aeration, either by cascading or spraying the water at the head of works or by bubbling air through the water passing through a contact chamber. Tastes can also be due to the presence of suspended solids in the water and these are normally removed in the settling and filtration stages of the works.

Other tastes are removed by reaction with oxidants and this can either take place through pre-oxidation which attempts to remove the tastes before coagulation, settling and filtration, or at the disinfection stage. Care should be taken at the final disinfection stage when using certain disinfectants, such as ozone, as this can lead to the formation of biodegradable compounds which cause problems in the distribution system, and the addition of chlorine after this may give rise to additional tastes in the water due to the reaction of compounds in the water with the chlorine. For example, chlorine reacts with phenols to give rise to chlor-phenol tastes and with tri-halomethane (THM) precursors to form THMs, which are also suspected carcinogens and therefore of concern from a health aspect too.

It is therefore preferable to remove the taste and odour compounds as early as possible in the treatment process. This is normally carried out by preoxidation, the purpose of which is to destroy compounds which give rise to tastes in the water, such as phenols, THM precursors and other organic compounds. This can be done with a number of oxidants such ozone; chlorine; chlorine dioxide; hydrogen peroxide with ozone (peroxone), potassium permanganate and various combinations of chemicals.

Ozone is generally the most effective oxidizing agent for removing tastes, however certain taste and odour compounds are not readily removed such as geosmin and 2-methylisoborneol (2-MIB) and in such cases removal by adsorption using powdered activated carbon (PAC), or granular activated carbon (GAC), is necessary. The use of PAC is discussed in Chapter 7.

6.3. PREOXIDATION

As discussed in the previous section, preoxidation is carried out to remove taste and odour compounds which may be present in the water. In addition to this, preoxidation also oxidizes inorganic compounds such iron and manganese which need to be corrected to the desired oxidation state for removal in the coagulation and flocculation process. Preoxidation also renders algae and related organisms amenable to coagulation by denaturing them or destroying them such that the residual material can be coagulated. A problem with this process is that the preoxidation stage may itself release certain taste and odour forming substances into the water. For this reason strong oxidizing agents need to be used in many cases to oxidize such taste

and odour compounds and, if possible, to avoid the need for dosage of powdered activated carbon.

Preoxidation at a works can be carried out in a number of ways. The simplest method, which is used for ground waters or impounded waters where dissolved oxygen may be absent, is to aerate the incoming water. The air strips out volatile compounds and the oxygen oxidizes some of the readily reactable organic compounds in the water. In other cases where stronger oxidising power is needed, the preoxidant is added to the water before the addition of coagulant and usually allowed to contact with the water for a suitable period before the other chemicals are added.

Ferrous iron is readily oxidized in the presence of air, but the oxidation of manganese is relatively slow and passes through a number of valence changes. Chlorine can be used to assist the oxidation of manganese, but this reaction is also relatively slow and the chlorine requires to be added as early in the process as possible if the manganese is to be removed on the filters. Raising the pH also assists the oxidation of manganese but if the presence of manganese at relatively high concentrations is an ongoing problem the use of other oxidants such as potassium permanganate, chlorine dioxide or ozone may be necessary. Ozone is the strongest oxidant but care in dosage control is necessary to avoid over-oxidising the manganese to permanganate. The generation of ozone has to take place on site and it entails relatively high capital cost. Where a strong oxidant is needed and ozone is not feasible, chlorine dioxide is a possible alternative.

6.4. DISINFECTION

Disinfection is the final stage of treatment before the drinking water is distributed. Disinfection removes pathogenic organisms, such as bacteria and viruses, from the water. However a water which has been disinfected is not sterile and does contain a number of harmless organisms.

The disinfection of water ideally requires 2 stages:

1. The first stage involves the removal of the pathogenic organisms from the water by the reactions taking place with the disinfectant.

2. The second effect required is the maintenance of the presence of a residual concentration of the disinfectant in the water that would then protect the reticulation system from re-infection and ensure that the water at the furthest point in the reticulation system remains safe for potable use.

Some disinfectants have very strong bactericidal effects and remove pathogenic organisms highly effectively, but do not have a residual effect and therefore cannot protect the reticulation system. For example ozone is highly effective in removing bacteria and viruses, but to protect the disinfection system with a residual requires the secondary addition of chlorine, chlorine dioxide or chloramines. The residual effect appears to be limited to halogens, usually chlorine based compounds. Chlorine itself has a residual which will last in a reticulation system at average dosage levels for approximately 48 hours. Chlorine dioxide has similar residual characteristics but can impart a taste to the water if the residual is too high. Monochloramine is often used at works with long reticulation systems, as chloramines can persist for 5 and even up to 10 days in certain circumstances. In such cases, the water is first disinfected beyond the chlorine breakpoint concentration to ensure effective disinfection and then ammonia, either in gaseous form or as a solution, is added to the water at ratios of between 3:1 to 6:1 chlorine to ammonia-N on a mass basis to form monochloramine. However, if the chlorine to ammonia ratio is too high, dichloramines and N-chloro compounds are formed which impart unpleasant tastes and odours to the water (White, 1992).

As mentioned earlier in this chapter, the addition of a disinfectant at the final treatment stage in a waterworks is intended to remove the pathogenic organisms. However, as the disinfectant is usually also a strong oxidizing agent, oxidation of compounds which have persisted through the treatment process can occur at the disinfection stage if no pre-oxidation has been carried out. A common problem in this regard is the deposition of manganese in reticulation systems where its presence in the raw water may not have been suspected and it is only oxidized at the chlorine disinfection stage at the end of the treatment process. A similar problem is the generation of taste and odour compounds at the chlorine disinfection stage where there has been no preoxidation. For this reason care should be taken to ensure that the water is adequately pre-oxidized and taste and odour substances and precursors removed before the final disinfection stage.

6.5. OXIDANTS

In this section we shall consider oxidants which are not necessarily disinfectants due to their relatively poor disinfecting ability.

6.5.1. AIR

Air is the most common oxidant and is used extensively in water treatment processes to strip out volatile compounds from the water and to initiate the oxidation of inorganic compounds where the water entering the plant may be anaerobic or limited in its available oxygen. The presence of dissolved oxygen in water as a result of aeration initiates a number of oxidation reactions, some of which are almost immediate whereas others are slow and might need the assistance of a stronger oxidant

6.5.2. OXYGEN

The use of pure oxygen is relatively rare, but is known in certain specialised cases where a higher partial pressure of oxygen will increase the rate of oxidation of certain compounds.

6.5.3. HYDROGEN PEROXIDE

Hydrogen peroxide is relatively unstable and releases oxygen in a slow process of decomposition. Although a stronger oxidant than air, it is not strong enough for most of the reactions required in potable water treatment and needs to be used at high dosages, which are generally not economically viable. It is used occasionally in swimming pools for removal of algae, but in potable water its use is largely confined to being a co-oxidant with ozone in the peroxone addition process.

6.5.4. POTASSIUM PERMANGANATE

Potassium Permanganate is used as an oxidant in certain specialised cases, particularly where manganese is present. The addition of permanganate converts the manganese that is in a reduced and soluble form to insoluble manganese dioxide, which can be removed by coagulation at the sedimentation stages.

6.6. DISINFECTANTS

In this section strong oxidizing agents that are also used for disinfection purposes are considered.

6.6.1. CHLORINE

Chlorine is by far the most common disinfecting agent used in water treatment. Its use is almost universal and has been practiced for approximately a hundred years. In its natural state chlorine is a greenish yellow gas with a specific weight of about 2½ times that of air, an atomic weight of about 35, and a boiling point of about minus 34°C at atmospheric pressure. Chlorine is an irritating and suffocating gas that is not corrosive in its pure dry state. However it is highly corrosive in the presence of even slight humidity and because of its high reactivity and oxidation potential the gas can produce explosive reactions with ammonia and hydrogen.

Chlorine is normally generated by electrolysis from sodium chloride (common salt) in a membrane plant and is supplied dried in liquid form under pressure in cylinders or drums. The most common method of chlorine addition is to use chlorine gas which is then dissolved in a carrier stream of water and added to the water to be treated. Care is required in the handling of chlorine as it is highly reactive and can destroy many organic compounds such as gasketing materials and sealants commonly used in engineering installations. Chlorine can also be added in solution form as sodium hypochlorite, which is produced by reacting together chlorine and sodium hydroxide generated from the electrolysis of salt. Sodium hypochlorite is normally added as a 15% (max.) solution or is diluted further before addition to the water. Whereas chlorine gas is acidic and reduces the pH of the water, sodium hypochlorite is alkaline and raises the pH. A third form of chlorine is calcium hypochlorite (HTH), which is a granular solid containing about 70% chlorine by weight. Although it is often used in

swimming pools, its use on waterworks is unusual because of the higher cost and greater difficulty in ensuring accurate dosage

Chlorine is added to the water at concentration levels sufficient to give a residual of approximately 0,5 mg/L with a contact time of about half an hour and a pH of preferably around 8 or less to ensure effective disinfection. The reaction of chlorine in water is such that its disinfecting ability is pH dependent and relates to the varying equilibrium concentrations of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-). The disinfecting ability of chlorine is better at low pH levels, but adequate results can be expected even at pH levels slightly above 8. The required contact time for adequate disinfection however increases as the pH increases.

As mentioned previously, the great advantage of chlorine is its ability to protect the reticulation system. The distribution system is protected by the residual effect of chlorine which persists through the reservoirs and pipework for periods in excess of 2 days. This is generally long enough for most installations.

6.6.2. CHLORAMINES

Chloramines are formed by the reaction of chlorine and ammonia under controlled conditions. In water treatment practice the formation and dosage of monochloramine is used for protecting the reticulation systems in large municipalities and installations. Monochloramine persists for a period of 5 to 10 days in the reticulation system which is useful where reservoir capacity is large or the reticulation system has been built in such a way that long retention times are required at the furthest reaches of the system. Monochloramine is generated by adding chlorine and ammonia to water in the ratio of approximately 3:1 up to 6:1 (chlorine to ammonia). The addition of ammonia is normally carried out after chlorine has been added and allowed to contact with the water for 15 to 30 minutes. This allows chlorine disinfection to take place before the residual effect of the chloramines is introduced to the water. Chlorine is a much stronger disinfectant than monochloramine.

6.6.3. CHLORINE DIOXIDE

Chlorine Dioxide has the formula ClO_2 and is normally generated from sodium chlorite ($NaClO_2$) using hydrochloric acid or chlorine gas. Chlorine dioxide is an explosive compound and is only safely handled if kept dissolved in water. Because of its explosive characteristics it is normally generated on-site from chlorine and chlorite in a liquid reactor. Chlorine dioxide is a stronger oxidant than chlorine under most circumstances and also has the advantage of forming a residual in the water, although this does not persist as long in the distribution system as does a chloramine residual. Chlorine dioxide is used where chlorine is an insufficiently strong oxidant to remove certain compounds from the water. It is normally used at dosage levels somewhat lower than that of chlorine and the reaction times are generally quicker. A dosage of approximately 0,2 mg/L for 15 minutes usually provides effective protection.

6.6.4. BROMINE

Bromine is also a strong disinfectant and is effective over a wider range of pH than chlorine. Because of costs, bromine use has generally been limited to disinfection of swimming pools and its use would not be recommended in conjunction with ozone due to the possible formation of bromates. Various suppliers have mooted the use of bromine for wastewater disinfection in this country, but caution is advised in the use of bromine for potable use.

6.6.5. OZONE

Ozone is one of the strongest oxidizing agents and disinfectants known. It is generated by electric discharge at relatively high frequencies in dry air or dry oxygen, and efficient generators can produce up to 14% ozone in an oxygen stream. Generation from air requires very careful air filtration and drying of the air as a dew point of -60°C to -70°C is required if arcing of electrodes in the ozone generator is to be avoided. Ozone is a gas at ambient temperatures and is highly reactive and toxic.

Ozone is relatively sparingly soluble in water and its addition to the treatment stream is therefore more difficult than that for chlorine. Addition to the water is usually through diffusers or at the throat of a venturi on a recycle side stream. Efficient contacting with the water is essential if the production of large quantities of waste

ozone requiring destruction is to be avoided. Unreacted ozone represents wastage of generation capacity and an additional cost to the treatment process.

In the early years of its use in water treatment, ozone was generally only added at the disinfection stage as a final disinfectant, sometimes supplemented with chlorine addition in order to provide a chlorine residual to protect the reticulation system. Over the years it has been discovered that the addition of ozone at such a late stage in the treatment process results in a breakdown of organic compounds, which allow further biological action in the reticulation system. The general practice today is to add ozone at a pre-oxidation stage to oxidize most of the organic compounds so that they break down through the water treatment process and do not cause complications in the distribution system. Ozone can therefore be added as pre-oxidation, intermediate oxidation or post disinfection.

As one of the strongest oxidants known ozone destroys bacteria and viruses more effectively than chlorine. However, its side effects and reaction products have not been researched as thoroughly as those of chlorine and the effects of its by-products are not as well known. Whereas it is known that chlorine gives rise to certain harmful by-products, we surmise that these may occur with ozone but the information has not been adequately documented at this stage. It is known however that ozone does generate certain aldehydes and ketones in the oxidation process, some of which can be harmful.

Ozone is used to oxidize various compounds as well as to disinfect, and markedly improves the taste and appearance of the treated water. For pre-oxidation purposes ozone dosages of around 1,5 to 3 mg/L are generally applied. For disinfection, a dosage of approximately 0,4 mg/L for 4 minutes (ct of 1,6) is recommended to remove pathogenic bacteria and viruses. Ozone is also effective against *Giardia* cysts and *Cryptosporidium* oocysts, as it inactivates the cysts and oocysts, which are resistant to attacks by chlorine.

6.7. MEASUREMENT OF DISINFECTANTS OR OXIDANTS

There are a number of specific tests for ozone, chlorine and other halogens that are discussed in the methods section of this report. For control purposes on a works however, the standard test would normally be the DPD coloration test, which is common to all the oxidants. It is therefore extremely difficult to separate the relative concentrations if mixed oxidants or disinfectants are being used. In practice however, this is not a serious limitation has normally one would be using a single oxidant or disinfectant. All that is required in this case is to multiply the result obtained from the reading on the colour disk or the spectrophotometer by the relevant factor for the particular chemical involved such as chlorine dioxide, chlorine, bromine or ozone.

Other important tests required for oxidants and disinfectants are demand tests. Generally these tests involve adding increasing increments of the oxidant or disinfectant to samples of the water to be tested. It is important that all treatment conditions, such as the method of disinfectant/oxidant addition, reaction vessel dimensions, pH, temperature and contact time are reported. After the specified contact time, the amount of residual disinfectant/oxidant is measured in each sample and in this way it is possible to determine the demand. For many of these chemicals, the demand is the applied dose at which a residual can still be measured after the specified contact time. However, in the case of chlorine, the applied dose needs to be higher than the break-point concentration. At doses lower than break-point, disinfection will not be as effective and the possibility of offensive odours and tastes exists and the chlorine residual consists predominantly of monochloramine, dichloramine and at certain chlorine to ammonia ratios, nitrogen trichloride. At concentrations higher than the break-point, the chlorine residual consists predominantly free chlorine. Research has indicated that maintaining a free chlorine residual that is at least 85% of the total chlorine residual prevents unpleasant tastes in the water and provides the best disinfection (White, 1992).

6.8. ANALYTICAL METHODS

6.8.1. CHLORINE

1. Introduction

Chlorination of water supplies serves primarily to destroy or deactivate disease-producing micro-organisms and to improve water quality by reaction with ammonia, iron, manganese, sulphide and some organic substances. Chlorination can also produce adverse effects, for example the taste and odour characteristics of phenols and other organic compounds present in a water supply may be intensified. It is important to be able to measure the concentration of chlorine in water and solution form. For low concentrations, DPD methods are suitable, but for more concentrated solutions, the dilutions required when using the DPD methods introduce inaccuracies into the determination. The iodometric titration procedure described in this method is ideal for waters and solutions in which the chlorine concentration is at least 1 mg/L, although usually higher, since the DPD methods are adequate for concentrations of up to 10 mg/L.

2. Scope

This method may be used to determine chlorine concentration in water and solutions provided that the concentration is at least 1 mg/L.

3. Interferences

Oxidised forms of manganese, other oxidising agents, organic sulphides and other reducing agents cause interferences. Ferric and nitrate ion interference is minimised at neutral pH, however the acid titration is preferred as some forms of combined chlorine do not react at pH 7. Acetic acid should be used in the titration, since sulphuric acid increases interferences and hydrochloric acid should never be used.

4. Hazards

1. Glacial acetic acid
2. Sulphuric acid
3. Potassium dichromate

Ensure that you are familiar with the dangers and treatment associated with each of the above substances.

5. Sample Collection

Samples may be collected in either amber or clear glass containers, preferably stored in the dark and analysed as soon as possible. If analysis cannot be conducted immediately, chill and store in the dark.

6. Apparatus

1. Burette
2. Volumetric equipment.
3. A-grade glassware.

7. Reagents

Use only distilled water.

All prepared solutions are made up in volumetric flasks and are stored in glass containers, unless otherwise indicated.

1. Glacial acetic acid concentrated
2. Sulphuric acid (concentrated)
3. Potassium iodide
4. 0,1 N Sodium thiosulphate
   - Dissolve 25g of $Na_2S_2O_3$. $5H_2O$ in 1 L of freshly boiled distilled water.
   - This should be stored for two weeks before use.
5. 0,01 N Sodium thiosulphate
   - Dilute 100 mL of 0,1 N $Na_2S_2O_3$ (10 x) into 1000 mL of freshly boiled distilled water.
6. 0,1 N Potassium dichromate
   - Dissolve 4,904 g of previously dried $K_2Cr_2O_7$ in 1 000 mL of distilled water.
   - Store in an amber bottle with a glass-stoppered lid.
7. 0,1 N Potassium dichromate
   - Dilute 100 mL of 0,1 N $K_2Cr_2O_7$ (10X) into 1 000 mL of distilled water.
   - Store in an amber bottle.
8. Starch indicator
   - Dissolve 5 to 15 g of soluble starch in 500 mL of distilled water. Keep refrigerated.

8. Analytical procedure

Exercise caution when handling chlorine. It is recommended that gloves be worn. Do not inhale nor ingest. Upon ingestion, proceed to hospital immediately. It is recommended that the sample be handled in a fume cupboard with the extractor fan running.

1. For sodium hypochlorite solutions of nominal 8 to 16% concentration, dilute the sample 1 000 times e.g. pipette 10,0 mL into a 100 mL volumetric flask and make to the mark using distilled water (10 x dilution). Pipette 10,0 mL of the 10 x dilution solution into a 1 000 mL volumetric flask and dilute to the mark using distilled water. For other solutions, dilute appropriately as above. Store diluted solutions in a dark cupboard.
2. Standardisation of 0,01 N $Na_2S_2O_3$.
   - Into a 250 mL conical flask pipette 10,0 mL of 0,01 N $K_2Cr_2O_7$.
   - Add 1 mL of concentrated sulphuric acid.
   - Add a spatula full of potassium iodide (KI) crystals.
   - Place in dark cupboard for 6 minutes.
   - Titrate against 0,01 N sodium thiosulphate until a pale straw colour is visible.
   - Add approximately 1 to 2 mL of starch indicator and the solution will turn deep blue-black. Titrate until colourless.
   - Record the volume of thiosulphate (mL).
   - Run blank titrations together with the standardisation titrations which contain all the reagents, except replace the 10,0 mL $K_2Cr_2O_7$ with distilled water.
3. Standardisation of chlorine sample.
   - Dilute the sample as described in (8)1 above.
   - Into a 500 mL conical flask measure 250 mL of the 1 000 times dilution of the chlorine sample.
   - Add 5 mL of glacial acetic acid.
   - Add a spatula full of KI crystals.
   - Immediately titrate against standardised 0,01 N sodium thiosulphate until a pale straw colour.
   - Add approximately 1 to 2 mL of starch indicator and the solution will turn deep blue-black. Titrate until colourless.
   - Record volume of thiosulphate.
   - Run blank titrations together with the standardisation titrations, replacing the 250 mL chlorine sample with 250 mL distilled water.

- Low concentrations of chlorine can also be read using the *N, N* – diethyl-p-phenylenediamine (DPD) method (see Method 6.8.7.).

9. Calculation

$$N\ (Na_2S_2O_3) = \frac{10 \times 0{,}01}{Na_2S_2O_3\ \text{Titre vol. (mL)}}$$

Concentration of Chlorine solution mg/L =

$$\frac{\text{Titre } Na_2S_2O_3\ \text{(mL)} \times 35\,450 \times \text{dilution} \times N\ (Na_2S_2O_3)}{250}$$

10. References

1. Standard Methods for the Examination of Water and Wastewater", 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.

6.8.2. CHLORINE DIOXIDE

1. Introduction

Chlorine dioxide is used to oxidise soluble iron and manganese to more easily removable forms and is used in water supplies to combat taste and odours due to phenolic-type wastes, actinomycetes and algae. It can also be used as a disinfectant, with physical and chemical properties that resemble those of chlorine although it is potentially a more powerful disinfectant than chlorine.

2. Scope

This method may be used to determine the concentration of chlorine dioxide in solution form.

3. Interferences

4. Hazards

1. Glacial acetic acid
2. Sulphuric acid
3. Potassium dichromate

Ensure that you are familiar with the dangers and treatment associated with each of the above substances.

5. Sample Collection

Samples may be collected in either amber or clear glass containers and should preferably be stored in the dark and analysed as soon as possible. If analysis cannot be conducted immediately, chill and store in the dark.

6. Apparatus

1. Burette
2. Volumetric equipment.
3. A-grade glassware.

7. Reagents

Use only distilled water. All prepared solutions are made up in volumetric flasks and are stored in glass containers, unless otherwise indicated.

1. Glacial acetic acid concentrated
2. Sulphuric acid concentrated
3. Potassium iodide
4. 0,1 N Sodium thiosulphate
   - Dissolve 25 g of $Na_2S_2O_3$. $5H_2O$ in 1 L of freshly boiled distilled water.
   - This should be stored for two weeks before use.
5. 0,01 N Sodium thiosulphate
   - Dilute 100 mL of 0,1 N $Na_2S_2O_3$ (10 x) into 1 000 mL of freshly boiled distilled water.
6. 0,1 N Potassium dichromate
   - Dissolve 4,904 g of previously dried $K_2Cr_2O_7$ in 1 000 mL of distilled water.
   - Store in an amber bottle with a glass-stopped lid.
7. 0,01 N Potassium dichromate
   - Dilute 100 mL of 0,1 N $K_2Cr_2O_7$ (10 x) into 1 000 mL of distilled water.
   - Store in an amber bottle.
8. Starch indicator
   - Dissolve 5 to 15 g of soluble starch in 500 mL of distilled water.
   - Keep refrigerated.

8. Analytical Procedure

Exercise caution when handling chlorine dioxide. It is recommended that gloves be worn. Do not inhale or ingest. Upon ingestion, proceed to hospital immediately. It is recommended that the sample be handled in a fume cupboard with the extractor fan running.

1. Dilute the sample 1 000 times (this is not always necessary, dilution may vary according to different samples) e.g. place 10,0 mL into a 100 mL volumetric flask and dilute to the mark using distilled water (this is a 10 x dilution).
   - Place 10,0 mL of the 10 x dilution into a 1 000 mL volumetric flask and dilute to the mark using distilled water.
   - Store in a dark cupboard.
2. Standardisation of 0,01 N $Na_2S_2O_3$
   - Into a 250 mL conical flask pipette 10,0 mL of 0,01 N $K_2Cr_2O_7$.

- Add 1 mL of concentrated sulphuric acid.
- Add a spatula full of potassium iodide (KI) crystals
- Place in dark cupboard for 6 minutes
- Titrate against 0,01 N sodium thiosulphate until a pale straw colour is visible
- Add approximately 1 to 2 mL of starch indicator and the solution will turn deep blue-black. Titrate until colourless.
- Record the volume of thiosulphate.
- Run blank titration together with the standardisation titrations, replacing the 10 mL $K_2Cr_2O_7$ with 10 mL distilled water.

3. Standardisation of chlorine dioxide sample
   - Dilute the sample as per (8)1 above, if necessary
   - Into 500 mL conical flask measure 250 mL of the 1 000 times dilution of the chlorine dioxide sample
   - Add 5 mL of glacial acetic acid
   - Add a spatula full of KI crystals
   - Immediately titrate against standardised 0,01 N or 0,1 N sohium thiosulphate until a pale straw colour.
   - Add approximately 1 to 2 mL of starch indicator and the solution will turn deep blue-black. Titrate until colourless.
   - Record volume of thiosulphate.
   - Run blank titrations together with the standard titrations, replacing the 250 mL sample or dilute sample with 250 mL distilled water.
   - Low concentrations of chlorine dioxide can also be read using the *N, N* – diethyl-p-phenylenediamine (DPD) method, to convert the reading to mg/L chlorine dioxide divide the reading by 2,63 (see Method 6.8.7.).

9. Calculation

$$N\ (Na_2S_2O_3) = \frac{10 \times 0{,}01}{\text{Titre } Na_2S_2O_3\ (mL)}$$

Concentration of chlorine dioxide solution mg/L=

$$\frac{\text{Titre } Na_2S_2O_3\ (mL) \times 13\,490 \times \text{dilution} \times N\ Na_2S_2O_3}{250}$$

10. References

1. “Standard Methods for the Examination of Water and Wastewater”, 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.

6.8.3. OZONE

1. Introduction

Ozone is an extremely powerful oxidant and disinfectant. It is more effective than ozone for inactivation of bacteria and viruses, although its side effects and reaction products have not been researched as thoroughly as those of chlorine and the effects of its by-products are not as well known. It is important that ozone concentrations can be measured since process ozone levels must be accurate in the water purification environment in order to ensure reliable and efficient product addition.

2. Scope

This method may be used to determine the concentration of ozone produced by an ozone generator.

3. Interferences

4. Hazards

1. Ozone gas: this has a characteristic smell and in small concentrations it is harmless, but if the concentration rises to above 100 mg/L, breathing becomes uncomfortable and it causes headaches.
2. Sulphuric acid (conc.).

Ensure that you are familiar with the dangers and treatment associated with each of the above substances.

5. Sample Collection

Samples must be titrated immediately after being collected.

6. Apparatus

1. Burette
2. Volumetric equipment.
3. A-grade glassware.

7. Reagents

Use only distilled water.

All prepared solutions are made up in volumetric flasks and are stored in glass containers, unless otherwise indicated.

1. Sulphuric acid conc.
2. Potassium iodide
3. Starch indicator (soluble)
4. 0,1 N Sodium thiosulphate
   - Dissolve 25 g $Na_2S_2O_3$. $5H_2O$ in 1 L of freshly boiled distilled water.
   - This should be stored for two weeks before use.
   - 0,01 N Sodium thiosulphate
   - Dilute 100 mL of 0,1 N $Na_2S_2O_3$ (10 x) into 1 000 mL of freshly boiled distilled water.
5. 0,1 N Potassium dichromate
   - Dissolve 4,904 g of previously dried $K_2Cr_2O_7$ in 1 000 mL of distilled water.
   - Store in an amber bottle with a glass-stoppered lid.
6. 0,01 N Potassium dichromate
   - Dilute 100 mL of 0,1N $K_2Cr_2O_7$ (10 x) into 1 000 mL of distilled water.
   - Store in an amber bottle.
7. Starch indicator
   - Dissolve 5 to 15 g of soluble starch in 500 mL of distilled water.
   - Keep refrigerated.

8. Analytical Procedure

1. Standardisation of 0,01 N $Na_2S_2O_3$
   - Into a 250 mL conical flask pipette 10,0 mL of 0,01 N $K_2Cr_2O_7$.
   - Add 1 mL of concentrated sulphuric acid.
   - Add a spatula full of potassium iodide (KI) crystals.
   - Place in dark cupboard for 6 minutes.
   - Titrate against 0,01 N sodium thiosulphate until a pale straw colour is visible.
   - Add approximately 1 to 2 mL of starch indicator and the solution will turn deep blue-black. Titrate until colourless.
   - Record the volume of thiosulphate.
   - Run blank titrations together with the standardisation titrations, replacing the 10,0 mL $K_2Cr_2O_7$ with 10,0 mL distilled water.
2. Standardisation of ozone sample

- Dilute the sample if necessary.
- Into 500 mL glass conical flask measure 2 mL of glacial acetic acid and 1 g of potassium iodide.
- Add the volume of ozone sample to be titrated.
- Immediately titrate against standardised 0,01 N or 0,1 N sodium thiosulphate until a pale straw colour.
- Add approximately 1 to 2 mL of starch indicator and the solution will turn deep blue-black. Titrate until colourless.
- Record the volume of thiosulphate.
- Run blank determinations together with the standardisation titrations, replacing the ozone sample with an equal volume of distilled water.
- Low concentrations of ozone can also be read using the *N, N* – diethyl-p-phenylenediamine (DPD) method. To convert the reading to mg/L ozone divide the reading by 1,48 (see Method 6.8.7.).

9. Calculation

$$N\ (Na_2S_2O_3) = \frac{10 \times 0{,}01}{\text{Titre } Na_2S_2O_3\ (mL)}$$

Concentration of ozone solution mg/L =

$$\frac{\text{Titre } Na_2S_2O_3\ (mL) \times 24\,000 \times \text{dilution} \times N\ (Na_2S_2O_3)}{\text{Volume ozone sample (mL)}}$$

10. References

1. "Standard Methods for the Examination of Water and Wastewater", 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.

6.8.4. ALTERNATIVE METHOD FOR OZONE DETERMINATION: INDIGO COLORIMETRIC METHOD

1. Introduction

The indigo colorimetric procedure provides a suitable method for measurement of low concentration ozone solutions. It also replaces methods like the iodometric procedure described in 6.8.3, which determines total oxidant rather than total ozone. The procedure is based on the principle that under acidic conditions, indigo is decolorised by ozone, the decrease in absorbance being linear with concentration. This method is suitable for use on a wide range of waters, including lakes, rivers, impoundments, manganese-containing groundwaters, very hard waters and biologically treated wastewaters.

2. Scope

This method may be used to determine the concentration of ozone present in a water, even in the presence of other oxidants.

3. Interferences

Hydrogen peroxide and organic oxides decolorise indigo very slowly, but if ozone measurements are made within 6 hours after addition of the reagents, then there is no interference from these. Organic peroxides also cause interferences, but these may react more quickly than hydrogen peroxide and organic oxides. Manganese (II) does not interfere, but it is oxidised by ozone to forms which decolorise the reagents. Corrections for this can be made by measuring a blank in which the ozone has been destroyed. Chlorine and bromine also cause interferences and at concentrations higher than 0,1 mg/L, an accurate ozone measurement cannot be made using this method. Low concentrations of chlorine can be masked with malonic acid.

4. Hazards

1. Phosphoric acid (conc.)

Ensure that you are familiar with the dangers and treatment associated with the above substance.

5. Sample Collection

Samples must be reacted with the reagents immediately after being collected. Once reacted with the reagents, spectrophotometric measurements should be made as soon as possible, but otherwise within 4 hours of reagent addition.

6. Apparatus

1. Spectrophotometer or filter colorimeter for use at 600 ±10 nm.
2. Volumetric glassware (100 mL and 1 000 mL)
3. A grade pipettes

7. Reagents

Use only distilled water.

All prepared solutions are made up in volumetric flasks and are stored in glass containers, unless otherwise indicated.

1. Phosphoric acid (conc.)
2. Sodium dihydrogen phosphate ($Na_2H_2PO_4$)
3. Indigo stock solution
   - Add approximately 500 mL distilled water and 1 mL conc. phosphoric acid to a 1 000 mL volumetric flask.
   - With stirring, add 770 mg potassium indigo trisulphonate, $C_{16}H_7N_2O_{11}S_3K_3$ (use only AR grade, commercially available at about 80 to 85% purity) and dilute to the mark with distilled water. A 1:100 dilution exhibits an absorbance of 0,20 + ±0,010 cm^{-1} at 600 nm. This solution is stable for about 4 months, but discard when absorbance of a 1:100 dilution drops below 0,16 cm^{-1}.
4. Indigo Reagent I
   - In a 1 000 mL volumetric flask, place 20 mL indigo stock reagent, 10 g sodium dihydrogen phosphate and ($Na_2H_2PO_4$) and 7 mL conc. phosphoric acid.
   - Dilute to the mark with distilled water.
   - Discard after 1 week.
5. Indigo Reagent II
   - Make up as for Indigo Reagent I, but use 100 mL Indigo Stock reagent instead of 20 mL.
6. Malonic Acid Reagent
   - Dissolve 5 g malonic acid in distilled water and dilute to 100 mL.

7. Glycine Reagent
   - Dissolve 7 g glycine in water and dilute to 100 mL.
8. Sodium Thiosulphate.

8. Analytical Procedure

1. For an ozone concentration range of 0,01 to 0,1 mg/L.
   - Add 10,0 mL indigo reagent I to each of two 100 mL volumetric flasks.
   - Fill one flask to the mark with distilled water or with sample in which the ozone has been destroyed using glycine reagent or a small quantity of sodium thiosulphate.
   - Fill the other flask to the mark with sample.
   - Measure the absorbance in both samples at 600 ± 10 nm preferably immediately, but within 4 hours (the more contaminated the water, the more important it is that the reading be made as soon as possible). Preferably use 10 cm cells.
2. For an ozone concentration range of 0,05 to 0,5 mg/L.
   - Proceed as for (8) 1 above, but use 10,0 mL of indigo reagent II, instead of indigo reagent I and preferably use 4 to 5 cm cells.
3. For ozone concentration ranges greater than 0,3 mg/L.
   - Proceed as for (8) 2 above using 10,0 mL of indigo reagent II, but use correspondingly smaller volumes of sample and then dilute sample and reagent mixture to the mark (100 mL) using distilled water.
4. Control of chlorine interference.
   - In the presence of low chlorine concentrations (<0,01 mg/L), place 1 mL malonic acid reagent into both flasks before adding sample, and measure absorbance as soon as possible (Br^{--}, Br_2 and HOBr are only partially masked by malonic acid).
5. Control of manganese interference using glycine solution.
   - Prepare a blank solution using sample in which the ozone has been selectively destroyed by adding 1,0 mL glycine reagent to one 100 mL flask and 10,0 mL indigo reagent II to the second and then adding equal volumes of sample to each flask adjusting the dose so that decolorisation in the second flask is easily visible, although complete bleaching is avoided (volume of sample must be less than 90 mL). Stopper flasks and mix by inverting.
   - Ensure that the pH of the contents of the first flask is higher than 6, since the ozone glycine reaction is very slow at low pH.

- 30 to 60 seconds after the addition of the sample to the first (blank) flask, add 10,0 mL indigo reagent II, stopper and mix thoroughly by inverting flask.
- Make both flasks up to the mark using ozone free water.
- Measure the absorbance in both flasks, using that of the blank flask as the blank reading in the calculation.

6. Control of manganese interference using sodium thiosulphate.
   - Conduct tests as described in (8)1, (8)2 or (8)3 above, but instead of preparing a blank using distilled water, use sample to which a few crystals of sodium thiosulphate has first been added.
7. Alternative Blank.
   - When measuring ozone concentrations in highly coloured and/or highly turbid waters, it is recommended that a sample of the water prior to ozonation be used for the blank, instead of distilled water, or better still, use ozonated water in which the ozone has been destroyed with sodium thiosulphate prior to addition of the indigo reagent. This compensates for interferences caused by colour and turbidity in the water. Ozone results in changes in colour, ultraviolet absorption (254 nm) and turbidity, even causing coagulation of particles in some cases. As a result, it is important that when measuring the ozone residual of polluted waters, the blank is an ozonated sample in which the ozone has been removed prior to addition to the indigo dye.

9. Calculation

$$\text{mg } O_3/L = \frac{100 \times \Delta A}{f \times b \times V}$$

Where:

ΔA = Difference in absorbance between sample and blank.

b = Path length of cell (cm).

V = Volume of sample (mL) (normally 90 mL)

f = 0,42 (proportionality constant of indigo reagent at 600 nm compared to UV absorption of pure ozone at 258 nm).

10. References

1. “Standard Methods for the Examination of Water and Wastewater”, 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.
2. Process Services, Umgeni Water.

6.8.5. HYDROGEN PEROXIDE

1. Introduction

The process in which hydrogen peroxide decomposes to release oxygen is slow and although it is a stronger oxidant than air, it is not strong enough for most of the reactions required in potable water treatment and needs to be used at high dosages, which are generally not economically viable. In potable water applications, it is usually used as a co-oxidant with ozone in the peroxone addition process.

2. Scope

This method may be somewhat less accurate than the permanganate titration, but it is less susceptible to interferences by organics, and is more suitable for measuring mg/L levels of H_2O_2.

3. Interferences

4. Hazards

1. Industrial grade Hydrogen peroxide
2. Sulphuric acid (conc.)

Ensure that you are familiar with the dangers and treatment associated with each of the above substances.

5. Sample Collection

Samples may be collected in either amber or clear glass containers and should preferably be stored in the dark and analysed as soon as possible. If analysis cannot be conducted immediately, chill and store in the dark.

6. Apparatus

1. Burette.
2. Volumetric equipment.
3. A-grade glassware.

7. Reagents

Use only distilled water. All prepared solutions are made up in volumetric flasks and are stored in glass containers, unless otherwise indicated.

1. Sulphuric acid (1:20)
2. Potassium iodide
3. Starch indicator (soluble)
4. 0,1 N Sodium thiosulphate
   - Dissolve 25 g of $Na_2S_2O_3$. $5H_2O$ in 1 L of freshly boiled distilled water.
   - This should be stored for two weeks before use.
5. 0,01 N Sodium thiosulphate
   - Dilute 100 mL of 0,1 N $Na_2S_2O_3$ (10 x dilution) into 1 000 mL of freshly boiled distilled water.
6. 0,1 N Potassium dichromate
   - Dissolve 4,904 g of previously dried $K_2Cr_2O_7$ in 1 000 mL of distilled water.
   - Store in an amber bottle with a glass-stopped lid.
7. 0,01 N Potassium dichromate
   - Dilute 100 mL of 0,1 N $K_2Cr_2O_7$ (10 x dilution) into 1 000 mL of distilled water.
   - Store in an amber bottle.
8. Starch indicator
   - Dissolve 5 to 15 g of soluble starch in 500 mL of distilled water.
   - Keep refrigerated.

8. Analytical Procedure

1. Dilute the H_2O_2 solution to a 0,3 % H_2O_2. If a commercially available solution of approximately 7 to 8% H_2O_2 is used, pipette 10,0 mL into a 250 mL volumetric flask and make to the mark. Shake.
2. Standardisation of 0,01 N $Na_2S_2O_3$
   - Into a 250 mL conical flask pipette 10,0 mL of 0,01 N $K_2Cr_2O_7$.
   - Add 1 mL of concentrated sulphuric acid.
   - Add a spatula full of potassium iodide (KI) crystals.
   - Place in dark cupboard for 6 minutes.
   - Titrate against 0,01 N sodium thiosulphate until a pale straw colour is visible.
   - Add approximately 1 to 2 mL of starch indicator and the solution will turn deep blue-black. Titrate until colourless.
   - Record the volume of thiosulphate.

- Run blank determinations together with the standardisation titrations, replacing the 10,0 mL $K_2Cr_2O_7$ with 10,0 mL of distilled water.

3. Standardisation of hydrogen peroxide sample
   - Dilute the sample if necessary.
   - Into 500 mL glass stoppered bottle measure 100 mL of the 1:20 sulphuric acid and 1 g of potassium iodide.
   - Gradually add 25 mL of the diluted hydrogen peroxide, stirring constantly
   - Stand this solution for 15 minutes in the dark.
   - Immediately titrate against standardised 0,01 N or 0,1 N sodium thiosulphate until a pale straw colour.
   - Add approximately 1 to 2 mL of starch indicator and the solution will turn deep blue-black. Titrate until colourless.
   - Record volume of thiosulphate.
   - Run blank determinations together with the standardisation titrations, replacing the 25,0 mL H_2O_2 with 25,0 mL of distilled water.
4. Low concentrations of hydrogen peroxide can also be read using the *N, N* – diethyl-p- phenylenediamine (DPD) method (see Method 6.8.7.). To convert the reading to mg/L hydrogen peroxide divide the reading by 2,09.

9. Calculation

$$N\ (Na_2S_2O_3) = \frac{10 \times 0{,}01}{\text{Titre } Na_2S_2O_3\ (mL)}$$

Concentration of H_2O_2 solution mg/L =

$$\frac{\text{Titre } Na_2S_2O_3\ (mL) \times 17\,000 \times \text{dilution} \times N\ (Na_2S_2O_3)}{\text{Volume } H_2O_2 \text{ sample } (mL)}$$

10. References

1 "Vogel's Textbook of Quantitative Inorganic Analysis", 4th Ed., Revised by Basset, J.; Denney, R. G.; Jeffery, G. H.; and Mendham, J.; Longman, 1993.

6.8.6. BROMINE

1. Introduction

Use of bromine in potable water is rare, but it is used for wastewater disinfection. Bromide is added in conjunction with chlorine, which in turns oxidises bromide to bromine. The greater reactivity of bromine with natural organic matter in water can be attributed to the greater solubility of bromine in water when compared to chlorine. The fact that bromine reacts more quickly than chlorine does however allow for shorter contact times when using bromine. Bromine has also been found to form trihalomethanes more readily than chlorine, which has negative implications for potable water treatment.

2. Scope

This method is similar to those described in Methods 6.8.1, 6.8.2, 6.8.3 and 6.8.4 and is more suitable for measuring mg/L levels of bromine. This method will measure total bromine residual, including bromamines.

3. Interferences

All other strong oxidants will interfere in this procedure. It is not possible to use this method to differentiate between bromine and other oxidants such as chlorine or hydrogen peroxide.

4. Hazards

1. Industrial grade Hydrogen peroxide
2. Sulphuric acid (conc.)

Ensure that you are familiar with the dangers and treatment associated with each of the above substances.

5. Sample Collection

Samples may be collected in either amber or clear glass containers, preferably stored in the dark and analysed as soon as possible. If analysis cannot be conducted immediately, chill and store in the dark.

6. Apparatus

1. Burette.
2. Volumetric equipment.
3. A-grade glassware.

7. Reagents

Use only distilled water. All prepared solutions are made up in volumetric flasks and are stored in glass containers, unless otherwise indicated.

1. Glacial acetic acid concentrated
2. Sulphuric acid concentrated
3. Potassium iodide
4. 0,1 N Sodium thiosulphate
   - Dissolve 25 g of $Na_2S_2O_3$. $5H_2O$ in 1 L of freshly boiled distilled water.
   - This should be stored for two weeks before use.
5. 0,01 N Sodium thiosulphate
   - Dilute 100 mL of 0,1 N $Na_2S_2O_3$ (10 x) into 1 000 mL of freshly boiled distilled water.
6. 0,1 N Potassium dichromate
   - Dissolve 4,904 g of previously dried $K_2Cr_2O_7$ in 1 000 mL of distilled water.
   - Store in an amber bottle with a glass-stopped lid.
7. 0,01 N Potassium dichromate
   - Dilute 100 mL of 0,1N $K_2Cr_2O_7$ (10 x) into 1 000 mL of distilled water.
   - Store in an amber bottle.
8. Starch indicator
   - Dissolve 5 to15 g of soluble starch in 500 mL of distilled water.
   - Keep refrigerated.

8. Analytical Procedure

1. For percentage strength bromine solutions, dilute the sample 1 000 times e.g. pipette 10,0 mL into a 100 mL volumetric flask and make to the mark using distilled water (10 x dilution). Pipette 10,0 mL of the 10 times dilution solution into a 1 000 mL volumetric flask and dilute to the mark using distilled water. Otherwise dilute as appropriate. Store diluted solutions in a dark cupboard.
2. Standardisation of 0,01 N $Na_2S_2O_3$.
   - Into a 250 mL conical flask pipette 10,0 mL of 0,01 N $K_2Cr_2O_7$.

- Add 1 mL of concentrated sulphuric acid.
- Add a spatula full of potassium iodide (KI) crystals.
- Place in dark cupboard for 6 minutes.
- Titrate against 0,01 N sodium thiosulphate until a pale straw colour is visible.
- Add approximately 1 to 2 mL of starch indicator and the solution will turn deep blue-black. Titrate until colourless.
- Record the volume of thiosulphate (mL).
- Run blank titrations together with the standardisation titrations that contain all the reagents, except replace the 10,0 mL $K_2Cr_2O_7$ with distilled water.

3. Standardisation of bromine sample.
   - Dilute the sample as described in (8)1 above.
   - Into a 500 mL conical flask measure 250 mL of the diluted bromine sample.
   - Add 5 mL of glacial acetic acid.
   - Add a spatula full of KI crystals.
   - Immediately titrate against standardised 0,01 N sodium thiosulphate until a pale straw colour.
   - Add approximately 1 to 2 mL of starch indicator and the solution will turn deep blue-black. Titrate until colourless.
   - Record volume of thiosulphate.
   - Run blank titrations together with the standardisation titrations, replacing the 250 mL bromine sample with 250 mL distilled water.
   - Low concentrations of bromine can also be read using the *N, N* – diethyl-p-phenylenediamine (DPD) method (see Method 6.8.7.).

9. Calculation

$$N\ (Na_2S_2O_3) = \frac{10 \times 0{,}01}{\text{Titre } Na_2S_2O_3\ (mL)}$$

Concentration of bromine solution mg/L =

$$\frac{\text{Titre } Na_2S_2O_3\ (mL) \times 79\,900 \times \text{dilution} \times N\ (Na_2S_2O_3)}{\text{Volume } Br_2 \text{ sample (mL)}}$$

10. References

1 White, G. C.; “Handbook of Chlorination and Alternative Disinfectants”, 3rd Edition, Pub. van Nostrand Reinhold, 1992.
2 “Standard Methods for the Examination of Water and Wastewater”, 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.
3 Process Services, Umgeni Water.

6.8.7. DPD COLORIMETRIC TESTS FOR CHLORINE, CHLORINE DIOXIDE, OZONE, HYDROGEN PEROXIDE AND BROMINE

1. Introduction

The *N, N* – diethyl-p- phenylenediamine (DPD) colorimetric procedures provide simple and accurate procedures for the measurement of chlorine and other oxidants when present in the concentration ranges in which they normally occur during typical water treatment processes. For higher concentrations, the iodometric titration procedures described above or other titration procedures are recommended. DPD, in the absence of iodide reacts with free chlorine, chlorine dioxide (to one fifth of its total available chlorine) and part of the available ozone, hydrogen peroxide, bromine, and bromamine to produce a red colour that can then be used to determine the concentration of these species. The subsequent addition of a small amount of iodide causes monochloramine and the remaining ozone fraction to react with DPD. Excess iodide addition to the mixture will also cause any dichloramines present to take part in the reaction. Using the DPD tests, it is possible, not only to determine a wide range of oxidants, but in some cases, to be able to differentiate between different species of an oxidant, such as free chlorine, monochloramines and dichloramines. However, it is not possible to differentiate between oxidants if analysing a solution containing two or more different oxidants, such as ozone and hydrogen peroxide.

2. Scope

This method provides a simple and accurate procedure for measuring chlorine, chlorine dioxide, ozone, hydrogen peroxide and bromine in water. However, it cannot be used to differentiate between mixtures of oxidants. This method is based on a colorimetric procedure for free and total chlorine determination with modifications to allow measurement of chlorine dioxide, ozone, hydrogen peroxide and bromine.

3. Interferences

All strong oxidants will interfere in this method; hence it cannot be used for the measurement of mixtures of oxidants or disinfectants. Sample colour and turbidity can cause interference in the measurement. Oxidised manganese and chromate in excess of 2 mg/L also cause interference in this method.

4. Hazards

5. Sample Collection

Samples should be analysed immediately, especially for chlorine, chlorine dioxide, ozone and bromine.

6. Apparatus

1. Colorimeter or photometer designed for use with DPD tablets.
2. Glassware: cuvettes or cells for use with colorimetric equipment.

7. Reagents

Use only distilled water. All prepared solutions are made up in volumetric flasks and are stored in glass containers, unless otherwise indicated.

1. DPD No. 1 and No. 3 tablets (DPD No. 4 tablets can be used where DPD No. 1 and No. 3 tablets are used simultaneously).
2. Potassium permanganate.
    - Prepare a stock solution containing 894 mg $KMnO_4$ in 1 000 mL distilled water.
    - Add 10,0 mL stock solution to a 100 mL volumetric flask and dilute to the mark with distilled water. 1 mL of this solution diluted to 100 mL with distilled water gives a chlorine equivalent of 1,00 mg/L when reacted with DPD.
    - Prepare a series of standards with chlorine equivalent concentrations ranging between 0,05 and 4 mg/L. Develop colour by adding a DPD No. 1 tablet, crushing and dissolving and reading the chlorine equivalent concentration on the colorimeter.

8. Analytical Procedure

1. Colorimeter:
    - Place 10 mL distilled water in the blank cell of the colorimeter.
    - Place 10 mL sample (or dilution) of sample in the other cell.
    - Place the correct colour test disc into the colorimeter.
    - Using a source of good daylight, or a specially designed artificial daylight source, rotate the disc until the colour of the blank cell matches that of the sample cell and record the reading as F.

- Add a DPD No. 3 tablet and allow to stand for 2 minutes before reading the colour development as described above in (8) 4 and record this reading as T.

2. Other photometric equipment:
   - If using photometric equipment especially designed for measuring chlorine or any of the other oxidants, follow the manufacturers' instructions.

9. Calculation

If using equipment designed for chlorine determination, use the factors given in the calculations below. If using photometric equipment specifically designed for measurement of the oxidant being measured, then use the actual readings.

Free chlorine	=	F mg/L as Cl_2
Total chlorine	=	T mg/L as Cl_2
Chlorine dioxide	=	5 x F mg/L as Cl_2 or (5 x F/2,63) mg/L ClO_2
Ozone	=	T/1,48 mg/L as O_3
Hydrogen peroxide	=	F/2,09 mg/L as H_2O_2
Bromine	=	F x 2,25 mg/L as Br_2 (this includes the bromamines).

10. References

1 "Standard Methods for the Examination of Water and Wastewater", 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.

2 Adams, D. B; Carter, J. M.; Jackson, D. H.; and Ogleby, J. W.; "Determination of Trace Quantities of Chlorine, Chlorine Dioxide, Chlorite and Chloramines in Water", *Proc. Soc. Wat. Treatment and Exam.*, 15, pp117 – 153, 1966.

3 Palin, A. T.; "Current DPD Methods for Disinfectant Residual Measurement", *JIWE*, 40, pp 501 – 510, Dec. 1986.

OXIDANTS AND DISINFECTANTS

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

STANDARDISATION OF 0,01 N SODIUM THIOSULPHATE				
Sample	**Sample Volume**	**Dilution**	**Titre Volume**	**N $Na_2S_2O_3$**
Blank				
Titre 1				
Titre 2				
Average (- blank)				

STANDARDISATION OF OXIDANT				
Sample	**Sample Volume**	**Dilution**	**Titre Volume**	**mg/L Oxidant**
Blank				
Titre 1				
Titre 2				
Average (- blank)				

DPD Method						
Sample	**Conversion factor**	**Dilution factor**	**Free Residual**	**Total Residual**	**pH**	**Temp °C**

OZONE: INDIGO COLORIMETRIC METHOD				
Sample	**Indigo volume**	**Sample volume**	**Abs**	**mg/L**

6.8.8. AMMONIA

1. Introduction

Ammonia is not an oxidant or disinfectant, but it is used in conjunction with chlorine during chloramination and therefore, a method to determine the strength of ammonia solutions is included in this section of the manual.

Chloramination, or the formation of chloramines, is used primarily to extend the lifetime of the disinfectant residual. Chlorine, on reaction with water at the pH values typically encountered in water treatment, forms predominantly hypochlorous acid and some hypochlorite ion, but the residual formed during chlorination usually lasts only a few hours and certainly less than 2 days. In large distribution systems, water may remain in the system for far longer periods than this, meaning that by the time the water reaches the most remote users of the system, regrowth problems may have occurred due to the lack of any disinfectant residual. Reacting the chlorine residual achieved after breakpoint chlorination with ammonia to form monochloramines can overcome this problem. Monochloramine is a far weaker disinfectant than chlorine, but provided that breakpoint chlorination has been achieved to ensure adequate disinfection, monochloramines can provide a residual effect that will last for up to 7 days.

2. Scope

This method may be used to determine the concentration of ammonia solutions used in water treatment.

3. Interferences

Poor sampling techniques and exposure to light can result in deterioration of the ammonia solution.

4. Hazards

1. Hydrochloric acid.
2. Sodium hydroxide.

Ensure that you are familiar with the dangers and treatment associated with each of the above substances.

5. Sample Collection

Samples may be collected in either glass or plastic containers. Store samples in the dark if not analysed immediately.

6. Apparatus

1. Burette
2. Volumetric equipment.
3. A-grade glassware.

7. Reagents

Use only distilled water.

All prepared solutions are made up in volumetric flasks and are stored in glass containers, unless otherwise indicated.

1. 0,1 N Hydrochloric acid
   - Add 8,9 mL of Hydrochloric acid to 1 000 mL volumetric flask and make to the mark, using distilled water.
2. 1,0 N Sodium hydroxide solution
   - Weigh out 40,00 g of sodium hydroxide pellets into a plastic beaker.
   - Dissolve carefully in distilled water as this is an exothermic reaction.
   - Transfer to a 1 L volumetric flask and dilute to the mark with distilled water.
3. 0,1 N Sodium hydroxide solution
   - Using the 1 N NaOH, measure 100,0 mL of the 1 N solution into a 1 000 mL volumetric flask and make to the mark using distilled water.
4. Methyl Red indicator
   - This is a standard indicator powder and is added as a dry reagent.

8. Analytical Procedure

Exercise caution when handling ammonia. It is recommended that gloves be worn. Do not inhale nor ingest. Upon ingestion, proceed to hospital immediately. It is recommended that the sample be handled in a fume cupboard with the extractor fan running.

1. When using 25% ammonia solution, dilute the sample 100 times e.g. pipette 10,0 mL into a 1 000 mL volumetric flask and dilute to the mark using distilled water. Otherwise dilute as appropriate.
2. Pipette 100,0 mL of 0,1 N HCL in a 250 mL Erlenmeyer flask.
3. Add 50,0 mL of 100 times dilution of 25% ammonia solution to the acid.
4. Add about 0,2 g of methyl red indicator (use the tip of the spatula) to the solution.
5. Titrate against 0,1 N NaOH until the colour changes from a deep purple – red colour to orange.
6. Record the volume of NaOH.

9. Calculation

$$(100 - T) \times 0{,}1 \times 17{,}03 = \mathbf{x}\ \text{mg}$$

Where:

T = NaOH titration volume (mL).

Then, if **x** mg is in 50 mL of a 100 x dilution:

$$NH_3\ \text{g/L} = \frac{\mathbf{x}\ \text{mg} \times 100}{50}$$

$$\%\ NH_3 = \frac{\mathbf{x}\ \text{mg} \times 10}{50}$$

10. References

1. Process Services, Umgeni Water.

AMMONIA

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

Ammonia					
Sample	**Volume**	**Dilution factor**	**Volume NaOH**	**Conc. NH_3 g/L**	**Conc. NH_3 %**

Specific gravity method			
Sample	**volume**	**Sample mass**	**% NH_3**

7. ACTIVATED CARBON

7.1. INTRODUCTION

Activated carbon was initially used in water treatment essentially for the removal of taste and odour compounds, but with more stringent limits for organic contaminants being imposed by the United States Environmental Protection Agency, the European Economic Community and other statutory bodies, the use of activated carbon is becoming much more wide spread in water treatment and water recycling.

In Southern Africa, powdered activated carbon (PAC) is used primarily for the removal of two algogenic taste and odour compounds, namely geosmin and 2-methylisoborneol (2-MIB). These occur mainly due to the presence of two *cyanobacteria* or blue-green alga genera, *Microcystis* and *Anabaena* (Wnorowski and Scott, 1992).

Activated carbon is produced from a variety of raw materials, although coal, wood and coconut are most commonly used in the manufacture of PAC for potable water treatment applications. The raw material first undergoes carbonisation or pyrolysis in which it is heated to a temperature below 700° C in the absence of air to form a char. The material is then activated using oxidising gases such as steam, carbon dioxide, air and oxygen or using chemicals at temperatures of up to 1000° C (Sanks, 1978; Water Purification Works Design, 1997). Activation can give rise to surface areas in excess of 2 000 m^2/g, although for potable water applications, activated carbon with a surface area in the region of 500 to 1 500 m^2/g is generally used. The physical properties of the carbon are dependent upon the raw material, as well as both the method and extent of activation used. In general, coconut tends to give rise to a dense structure containing only a few larger pores, while wood-based activated carbon has an open structure with many more larger pores. The coal-based carbon usually has a structure somewhere between that of coconut- and wood-based carbons (Greenbank, 1992). Experience has shown that coal-based and wood-based carbons are usually more effective for water treatment applications.

It is the high degree of porosity and the large surface area that accounts for the adsorptive properties of activated carbon and by changing the activating conditions, the size and number of pores can be controlled to produce a carbon suited to a particular application (Sanks, 1978). The pores in activated carbon are generally divided into two classes depending on size, these being the micropores and the macropores, but the ranges quoted in the literature vary between <1 and 100 nm for micropores and anything from >10 to >100 nm for the macropores (Chemviron, 1974; Gregg and Sing, 1982; Sanks, 1978; Water Purification Works Design, 1997). The micropores are responsible for most of the surface area providing activated carbon with its adsorptive properties and in water grade carbons more than 70% of the of the available surface area is attributed to pores having a radius of less than 5 nm. Generally the external surface area of a typical water treatment PAC is insignificant compared to the surface area contained within the pores and therefore reducing the particle size, for example by grinding, will have a negligible effect on the total surface area (Sanks, 1978). In fact, the same is true of GAC and once ground, the same tests used to assess PAC can be used to assess GAC as well.

7.2. PAC VERSUS GAC

Both powdered and granular activated carbon (PAC and GAC) can be used for the adsorption of contaminants present in water, the main difference between the two being the particle size. Typically between 60 and 90% of the PAC particles pass through a 325 mesh (± 45 µm) sieve (Water Quality and Treatment, 1990).

PAC is usually used for the control of seasonal or sporadic incidents and can be added to the water at a number of sites, the most common being at the influent or the rapid mix section, although it can also be added to the flocculation basin influent or at the filter influent (Water Quality and Treatment, 1990). Plants using PAC doses of up to 50 mg/L can be found in the literature (Water Quality and Treatment, 1990), but not all plants can tolerate such high doses. Depending on the treatment train, coagulant dose and other factors, the amount of PAC which can be dosed on a plant may be less than half this before carryover from the clarifiers occurs.

GAC is generally more expensive than PAC treatment in that a large capital outlay is required, but it is also more effective than PAC in removing organic compounds, since GAC is usually preceded by pre-treatment which reduces the load on the

carbon. In spite of this PAC has a number of advantages over GAC, the main ones being the low capital cost of PAC and the ability to apply it only when it is needed (Najm *et al*, 1990). This is particularly important in a country like South Africa where outbreaks of taste and odour compounds are usually seasonal and intermittent.

The advantage of GAC becomes evident when carbon addition is required over extended periods of time. PAC is not regenerated as a rule and therefore becomes very costly when used for long periods. It also provides a lower rate of NOM removal than GAC, creates more sludge disposal problems and difficulties are often experienced in removing the PAC particles from the water (Sontheimer, 1976).

7.3. LABORATORY TESTING OF ACTIVATED CARBON

For laboratory testing of activated carbon, isotherm tests are commonly conducted in which reductions in target contaminants are measured at different carbon concentrations and after a specific contact time. These tests tend to be rather laborious and they often involve complicated adsorption models, apart from the fact that they generally provided nothing more than a rough estimate of the suitability of the carbon for the intended application. A number of isotherm-type tests has been developed over the years for the purpose of assessing the “acceptable” activity level of a carbon, such as iodine number, methylene blue number, phenol value, molasses number and tannin number. These tests are in some cases more rapid than the standard isotherm tests, but are often meaningless in determining the suitability of a carbon in meeting the treatment objectives. They are however useful indicators for quality control, allowing assessment of the degree of consistency between production batches.

7.3.1 IODINE NUMBER

The iodine number is defined as the milligrams of iodine adsorbed by one gram of carbon when the iodine concentration is 0,02 N (American Society of Testing and Materials [ASTM] D4607). Although the iodine number is useful as a quality control parameter for comparing different production batches of activated carbon, its value is fairly limited in determining whether or not a PAC is suitable for a certain treatment objective. The problem with this test is that iodine is a small molecule that is well adsorbed and the test is conducted at high iodine concentrations, resulting in a loading that is much higher than that encountered in practice. For example, the iodine

number specified for Chemviron Fitrasorb 400 (a GAC) is 1050 mg/g which is equivalent to a weight loading of 105% w/w, while the typical loading achieved in most liquid phase applications is less than 20% w/w (Chemviron, 1998). The iodine number test described in this manual is a combination of the ASTM D4607 three-point isotherm test and a simpler single-point isotherm test. The single-point isotherm test is not as accurate as the ASTM three-point isotherm test, but it allows for a far more rapid determination of the concentration range required for the three-point isotherm test. It is possible to eliminate Part A of the test if the concentration range required for the three-point isotherm test is known, but if not, Part A can be very time-saving, obviating the need for multiple repetitions of Part B .

7.3.2 METHYLENE BLUE

This test measures the capacity of an activated carbon to decolorise methylene blue and is also a measure of adsorption capacity. Two different types of methylene blue tests can be used. The first is the Chemviron Carbon method (TM-11) (Chemviron, 1998) and is similar to the iodine number. It involves adding a measured amount of activated carbon to a standard methylene blue solution. The methylene blue number is determined from the reduction in colour and is quoted in milligrams per gram. The other test procedure, which is the CEFIC Test Method (European Council of Chemical Manufacturers' Federations, 1986), involves the addition of a standard methylene blue solution to a sample of activated carbon until no further colour reduction occurs and the figure is then quoted in millilitres per gram (Chemviron, 1998). Whichever procedure is used, the methylene blue number, like the iodine number, provides only an indication of the adsorption potential of the carbon and usually has only limited value in assessing the PAC in terms of operational performance. The Chemviron TM-11 method is described in this manual.

7.3.3 PHENOL NUMBER

There are three different phenol number tests. There is an isotherm method which is contained in the German Standard DIN 19603 and is defined as the adsorption of phenol (in % w/w) on the activated carbon required to reduce the phenol concentration from 10 mg/L to 1 mg/L. There are also two American Water Works Association (AWWA) methods, one for PAC and the other for GAC. The PAC (AWWA

B600-96) method is also an isotherm test, similar to the DIN method, except that it is carried out at a much higher phenol concentration, the test requiring that the phenol concentration be reduced from 200 mg/L to 20 mg/L (Chemviron, 1998). In both tests, the lower the phenol number the better the adsorption potential of the carbon. As with the iodine number and methylene blue number tests, it is difficult to translate the phenol number into plant performance. Not only is the loading of phenol during the test much higher than for most contaminants that occur in water, but the phenol number value is also affected by pH.

7.3.4 TANNIN NUMBER

The tannin number test is an AWWA method (AWWA B600-78, revised in ANSI/AWWA B600-90, 1991 and again in ANSI/AWWA B600-96, 1996) and the tannin number is defined as the concentration of activated carbon in milligrams per litre required to reduce the standard tannic acid concentration from 20 mg/L to 2 mg/L.

A major disadvantage with isotherm tests is that although they provide an estimation of the PAC consumption and indicate whether a compound is adsorbable or not, they don't provide any design information, such as the required contact time. The isotherm tests described above are generally taken to equilibrium or are reacted for periods of time far greater than the contact time that the carbon has in typical water treatment and water reuse applications. This is one of the main reasons why these isotherm tests do not correlate well with full-scale operation. The total absorbing capacity of a carbon gives no indication of the kinetics of the adsorption reaction and since activated carbon generally has not more than 2 hours contact time with the water under typical water treatment conditions, the rate of adsorption is critical. It was for this reason that a number of major water treatment authorities in South Africa (the City of Cape Town, Rand Water and Umgeni Water) devised practical jar test-type tests capable of accounting for the contact time, as well factors such as the background organics, the treatment process and the effect of the other process chemicals on the PAC's potential for adsorption of contaminants. These tests, although all devised in-house and all differing in various aspects, have been found to correlate well, not only with full-scale treatment, but also with each other. Rand Water, Umgeni Water and the City of Cape Town recently collaborated on a Water Research Council research project investigating the suitability of powdered activated carbon for full-scale treatment applications (WRC Report No. K5/1124, 2003), during

which these tests were found to exhibit excellent correlation. All three tests are described in this manual.

7.3.5 ASH CONTENT

The ash content is of some significance, since constituents giving rise to ash will not possess any adsorption capacity. In other words, the ash content indicates inactive matter present in the carbon and can be an indication of a low grade carbon. Obviously if a carbon performs well in the jar test-type tests, then the ash content is less important, but whenever possible, carbon containing a high ash content should be avoided. The ash test described in this manual is the ASTM D 2866-83 (reapproved 1988) “Standard Test Method for Total Ash Content of Activated Carbon”, 1988.

7.3.6 MOISTURE CONTENT

The moisture content of activated carbon is often required to define and express its properties in relation to the net weight of the carbon. High moisture content is undesirable, since this will add to transport and storage costs and also, since moisture does not provide an adsorptive capacity, it should preferably remain low. It can also be an indication of poor storage conditions, which may have allowed the carbon to adsorb moisture from the atmosphere. The test moisture described in this manual is the ASTM D 2867-83 (Reapproved 1988) “Standard Test Methods for Moisture in Activated Carbon”, 1988.

7.4. ANALYTICAL METHODS

7.4.1 IODINE NUMBER

1. Introduction

The iodine number is a relative indicator of porosity in an activated carbon. It does not necessarily provide a measure of the carbon's ability to absorb other species. Iodine number may be used as an approximation of surface area for some types of activated carbons and it can be used to determine consistency between different batches or deliveries of a carbon. The presence of adsorbed volatiles, sulfur, and water extractables may affect the measured iodine number of an activated carbon.

2. Scope

This test method covers the determination of the relative activation level of unused or reactivated carbons by adsorption of iodine from aqueous solution. The amount of iodine absorbed (in milligrams) by 1 g of carbon using the test conditions described, is called the iodine number.

This method has two parts: the result from Part A allows for fairly rapid estimation of the concentration range required for Part B. Part B is a more accurate measure of the iodine number, using a three-point isotherm procedure.

Note:

It is not necessary to complete Part A to obtain the iodine number but experience has shown that it can reduce the work load considerably and allow for an overall more rapid determination of the iodine number.

3. Interferences

4. Hazards

1. Hydrochloric Acid

Ensure that you are familiar with the dangers and treatment associated with Hydrochloric Acid.

5. Sample Collection

Samples may be collected in plastic bags or in plastic containers.

6. Apparatus

1. Burette
2. A-Grade Pipettes
3. Beakers
4. Conical flasks 250 mL
5. Glass funnels
6. Graduated measuring cylinders
7. Whatman No. 2V filter paper or equivalent
8. Whatman No. 3 filter paper or equivalent
9. Analytical Balance

7. Reagents

1. 5% Hydrochloric Acid
    - Add 70 mL of conc. Hydrochloric acid to 550 mL of distilled water, and mix well
2. 0,1 N Sodium Thiosulphate
    - Dissolve 24,82 g of sodium thiosulphate in approximately 75 mL of freshly boiled distilled water.
    - Add 0,1 g of sodium carbonate to minimise bacterial decomposition of the thiosulphate solution.
    - Quantitatively transfer the mixture to a 1 L volumetric flask and dilute to the mark. Allow the solution to stand for at least 4 days before standardising. The solution should be stored in an amber bottle.
3. 0,1 N Iodine
    - Weigh 12,7 g of iodine and 19,1 g of KI into a beaker and mix the dry iodine and potassium iodide.
    - Add 2 to 5 mL of water to the beaker and stir well. Continue adding small increments of water, while stirring, until the total volume is 50 to 60 mL.
    - Allow the solution to stand a minimum of 4 hr to ensure that all the crystals are thoroughly dissolved.
    - Quantitatively transfer to a 1 Ll volumetric flask and fill to the mark with distilled water. Store the solution in an amber bottle.
4. Potassium Iodide
5. Starch

6. Sodium Carbonate
7. Sulphuric acid
8. 0,1 N Potassium dichromate
    - Weigh out 4,940 g potassium dichromate (previously dried to constant weight at 105° C, cooled and stored in a desiccator) into a beaker.
    - Quantitatively transfer to a 1 L volumetric flask and make to the mark.

8. Analytical Procedure

1. This procedure can be used for both powdered and granular activated carbons. Granular carbon must be ground until at least 95 wt% passes through a 325 mesh (50 µm) screen. Powdered carbons may also require additional grinding in order to meet this size requirement.
2. Standardisation of 0,1 N Sodium Thiosulphate
    - Pipette 10 mL of 0,1 N potassium dichromate into a 250 mL conical flask.
    - Add 90 mL of distilled water, 1 mL of concentrated sulphuric acid, and a spatula tip of KI.
    - Place in a dark cupboard for 5 minutes. Titrate against 0,1 N sodium thiosulphate, using starch as indicator.
3. Standardisation of 0,1 N Iodine
    - Pipette 20 mL of ± 0,1 N Iodine into a 250 mL conical flask. Titrate against standardised sodium thiosulphate, using starch as indicator.
4. Grind a representative sample of carbon until 95% or more will pass through a 50 µm sieve.
5. Dry the carbon in a 110° C oven for 3 hours.

Part A: Iodine Number (Single-point Isotherm)

6. Weigh out approximately 1 g of carbon into a 250 mL conical flask.
7. Add 10 mL of 5% hydrochloric acid, and swirl until the carbon is wetted.
8. Place the flask on a hotplate, and bring the contents to the boil for 30 seconds only.
9. Allow to cool to room temperature and then add 100 mL of standardised Iodine.
10. Immediately stopper the flask, and shake vigorously for 30 seconds.
11. Filter through a Whatman No. 3 filter immediately after shaking.
12. Discard the first 20 to 30 mL and collect the remainder of the filtrate in a clean conical flask.
13. Transfer 50 mL of this filtrate to a clean conical flask, and titrate the sample with the standardised sodium thiosulphate, using starch as indicator.

14. Calculate the estimated iodine number (E), using the attached graph.

Part B: Iodine Number (Three-point Isotherm).

15. Using three masses of carbon spanning the expected concentration range required (use the iodine number, E determined in Part A to estimate these three masses) add 10 mL of 5% hydrochloric acid to each, and swirl until the carbon is wetted.
16. Place the three flasks on hotplates, and bring the contents to the boil for 30 seconds only.
17. Allow to cool to room temperature and then add 100 mL of standardised 0,1 N iodine to each flask.
18. Immediately stopper each flask, and shake vigorously for 30 seconds.
19. Filter the contents of each flask through Whatman 2V (**NB. Note that Whatman 2V filters are used for Part B and not Whatman No. 3 filters**) immediately after shaking.
20. Discard the first 20 to 30 mL from each flask and collect the remainder of the filtrates in clean conical flasks.
21. Transfer 50 mL of each filtrate to clean conical flasks, and titrate each sample with standardised sodium thiosulphate, using starch as indicator.

9. Calculations

$$N\ (Na_2S_2O_3) = \frac{10 \times 0{,}1}{\text{Titre } Na_2S_2O_3\ (mL)\ (\text{Part A})}$$

$$N\ (I_2) = \frac{\text{Titre } Na_2S_2O_3\ (mL)\ (\text{Part A}) \times N\ (Na_2S_2O_3)}{20}$$

Part A:

$$N\ (I_2)\ (\text{Residual filtrate}) = \frac{N\ (Na_2S_2O_3) \times \text{Titre } Na_2S_2O_3\ (mL)\ (\text{Part A})}{50}$$

N (I_2) (Residual filtrate) is used to obtain F, the correction factor from the iodine correction graph (**Figure 7.1**) below.

$$E_{Part\ A} = \frac{F \times A - (DF \times B \times Titre\ Na_2S_2O_3\ (mL))}{Sample\ mass\ (g)}$$

Where:

$E_{Part\ A}$ = Iodine Number calculated from Part A

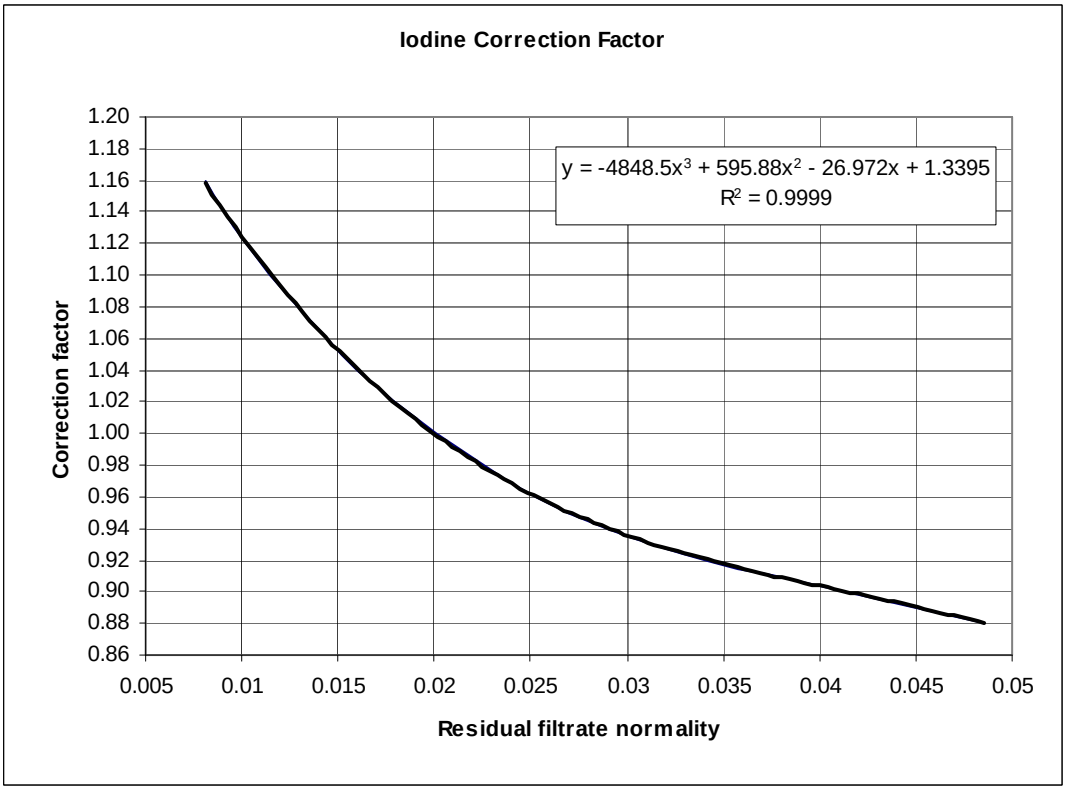
A = N (I_2) x 12693,0

B = N ($Na_2S_2O_3$) x 126,93

F = Correction factor obtained from iodine correction graph

DF = Dilution Factor = $\frac{100\ mL\ I_2 + 10\ mL\ HCl}{50}$ = 2,2

Figure 7.1: Iodine Correction Curve



Part B:

Estimation of the three carbon doses:

Use N (I_2) residual filtrate as the middle of a range of three residual filtrate normalities to calculate the three carbon doses.

Estimated masses for Part B (g) =

$$\frac{A - (13\,962{,}3 \times \text{residual filtrate normality [in this case 0,01; 0,02 or 0,03]})}{E_{\text{Part A}}}$$

After obtaining the 3 estimated doses, continue with **Part B**:
Calculate X/m (iodine adsorbed per gram of carbon), for each mass:

$$X/m = \frac{A - (2{,}2 \times B \times \text{Titre } Na_2S_2O_3 \text{ (mL)})}{\text{Sample mass (g)}}$$

Calculate C, the residual filtrate normality:

$$C = \frac{N\ (Na_2S_2O_3) \times \text{Titre } (Na_2S_2O_3) \text{ (mL)}}{50}$$

Plot C (as the abscissa) against X/m (as the ordinate) as a logarithmic graph for each of the three carbon dosages. Calculate the least squares fit for the three points. The Iodine Number is the X/m value at a residual iodine concentration of 0,02N. The regression coefficient for the least squares fit should be greater than 0,995.

10. References

1. Process Services, Umgeni Water.
2. ASTM D4607- 86

IODINE NUMBER

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

STANDARDISATION OF 0,1 N SODIUM THIOSULPHATE				
Sample	**Sample Volume**	**Dilution**	**Titre Volume**	**N $Na_2S_2O_3$**
Blank				
Titre 1				
Titre 2				
Average (- blank)				

STANDARDISATION OF 0,1 N IODINE				
Sample	**Sample Volume**	**Dilution**	**Titre Volume**	**N Iodine**
Blank				
Titre 1				
Titre 2				
Average (- blank)				

PART A: SINGLE POINT ISOTHERM			
Sample	**Mass (g)**	**Volume (mL)**	**E**

PART B: THREE-POINT ISOTHERM				
Sample	**Mass (g)**	**Xm**	**Volume (mL)**	**C**

7.4.2 METHYLENE BLUE NUMBER

1. Introduction

The methylene blue absorption test reveals the adsorptive properties of a carbon towards a larger molecule, and can give an indication of the internal surface area of the carbon. Like the iodine number, the methylene blue number is usually unsuitable for assessing an activated carbon in terms of treatment objectives, but it is useful for evaluating consistency between production batches of carbon.

2. Scope

This method is used for the determination of the methylene blue value for activated carbon.

3. Interferences

4. Hazards

Dust: activated carbon is an electrical conductor and should not be allowed to accumulate near or on open electrical circuits.

5. Sample Collection and Preservation

Samples may be collected in either plastic or glass containers or packets. Granular activated carbon is pulverised (<0,1 mm) and then dried at 150° C to constant weight.

6. Apparatus

1. Whatman 44 or No 3 filter paper
2. Analytical balance.
3. Spectrophotometer
4. Volumetric flasks

7. Reagents

1. Acetic acid 0,25%
    - Add 2,50 mL of glacial acetic acid to 900 mL of distilled water. Dilute to 1 L in a volumetric flask.
2. Standard Methylene Blue solution (1 200 mg/L)

- Weigh out 1,20 g methylene blue (previously dried to a constant weight, cooled and stored in a desiccator).
- Dissolve in 100 mL 50% acetic acid.
- Dilute to 1 L in a volumetric flask

3. Working methylene blue standards
   - Prepare a 120 mg/L intermediate methylene blue standard by diluting the stock 1:10 with 0,25% acetic acid into 100 mL volumetric flasks.
   - Pipette 10,0; 7,5; 5,0; and 2,5 mL of the intermediate methylene blue standard into each of four 100 mL volumetric flasks and make up to volume with 0,25% acetic acid. These standards are equivalent to residual methylene blue concentrations of 12 000, 9 000, 6 000 and 3 000 µg/L.

8. Procedure

1. Granular carbon must be ground until at least 95wt% passes through a 325 mesh (50 µm) screen. Powdered carbons may also require additional grinding in order to meet this size requirement.
2. Set the wavelength of the spectrophotometer to 620 nm and using a 10 mm cell read the working standards and record the absorbances.
3. Plot a calibration curve of methylene blue concentration versus absorbance and calculate the slope of the regression line.
4. Weight out 0,100 g of dried, ground carbon sample into a 100 mL beaker.
5. Add 25,0 mL of 1 200 mg/L methylene blue solution and stir on a mechanical stirrer for 30 minutes.
6. Filter through Whatman 44 or No 3 filter paper and discard the first 5 mL of filtrate.
7. Measure the absorbance of the filtrate at 620 nm (this gives R, the residual methylene blue concentration from the calibration curve).

9. Calculation

Methylene Blue absorption g/100g carbon = $\left(\frac{30 - R}{40}\right)$

Where:

R = residual methylene blue concentration.

10. References

1. Process Services, Umgeni Water.
2. European Council of Chemical Manufacturer' Federations (CEFIC), Test Methods for Activated Carbon, Belgium, 1986.

METHYLENE BLUE NUMBER

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

STANDARDS	
Standard (µg/L)	**Absorbance @ 620 nm**

DETERMINATION OF METHYLENE BLUE NUMBER			
Sample	**Mass Carbon (g)**	**Absorbance**	**MB Number**

7.4.3 PHENOL VALUE

1. Introduction

The phenol value test described here is defined as the concentration of activated carbon in grams per litre required to reduce the standard phenol concentration from 200 mg/L to 20 mg/L. The phenol value or number, like the iodine and methylene blue numbers is not of great value in assessing activated carbons in terms of plant performance, but can be useful for quality control purposes.

2. Scope

This method is used for the determination of the phenol value for powdered activated carbon. The phenol value can be used as an indicator of the activated carbon's ability to remove low-molecular-weight impurities.

3. Interferences

4. Hazards

Dust: activated carbon is an electrical conductor and should not be allowed to accumulate near or on open electrical circuits.

5. Sample Collection and Preservation

Samples may be collected in either plastic or glass containers or packets.

6. Apparatus

1. Whatman 2V filter paper
2. Analytical balance.
3. Iodine flasks
4. Erlenmeyer flasks
5. Spectrophotometer
6. 10 mm quartz cells
7. 200 mL volumetric flasks

7. Reagents

1. Stock phenol solution
    - Weigh 1,0 g of reagent grade phenol into a glass beaker.
    - Transfer to a 1 L volumetric flask and make to mark. Rinse the beaker well.
    - Discard solution after two weeks.
    - Remember to store reagent grade phenol in the refrigerator.
2. 0,1 N Sodium thiosulphate
    - Place 25 g $Na_2S_2O_3.5H_2O$ in a 1 L volumetric flask and dissolve in freshly boiled distilled water. Make up to the make with boiled distilled water. Store in an amber bottle. Standardise before use.
3. 0,1 N Potassium bromate-bromide
    - Dissolve 2,784 g of potassium bromate and 10,0 g of potassium bromide (bromate free) in distilled water and dilute to 1 L. Store in and amber bottle.
4. Potassium iodide crystals
5. Starch solution
6. Sulphuric acid
7. 0,1 N Potassium dichromate
    - Weigh out 4,940 g potassium dichromate (previously dried at 105° C to constant weight, cooled and stored in a desiccator) into a beaker.
    - Quantitatively transfer to a 1 L volumetric flask and make to the mark.
8. Buffer solution (8 strength)
    - Dissolve 728 g of anhydrous disodium phosphate (Na_2HPO_4) or equivalent weight of crystalline phosphate, in 2 L of hot distilled water.
    - When the phosphate is completely dissolved, acidify with approximately 100 mL of phosphoric acid, check using a pH meter, and make up to 7 L. Final pH should be 6,5.
    - Single strength buffer solution is prepared by diluting 100 mL of 8 strength buffer solution with 700 mL of distilled water.

8. Procedure

1. Standardisation of phenol solution
    - Pipette 25 mL of stock phenol solution into a 500 mL iodine flask.
    - Add 25 mL of potassium bromate-bromide using either a burette or pipette.
    - Shake flask.
    - Add 5 mL concentrated HCL.
    - Wait 3 minutes.
    - Add 8 mL of 12.5% KI.
    - Stand for 3 minutes, and then titrate the liberated iodine with ±0,1 N sodium thiosulphate, using starch as an indicator.
2. Standardisation of 0,1 N Sodium Thiosulphate
    - Pipette 10 mL of 0,1 N potassium dichromate into a 250 mL conical flask.
    - Add 90 mL of distilled water, 1 mL of concentrated sulphuric acid, and a spatula tip of KI.
    - Place in a dark cupboard for 5 minutes. Titrate against 0,1 N sodium thiosulphate, using starch as indicator.

Phenol test

1. Prepare a 200 mg/L phenol test solution by diluting one volume of stock phenol (1 000 mg/L) with four volumes of single strength buffer solution i.e. for 1 L of phenol test solution dilute 200 mL of stock phenol with 800 mL of single strength buffer solution. If the stock phenol solution concentration is not exactly 1 g/L adjust the volume used so that the test solution is maintained at 200 mg/L phenol.
2. **Enough test phenol solution must be prepared to conduct all the samples for the day** (200 mL per each carbon dose).
3. Use the activated carbon as received and determine the moisture content. (see method).
4. For each carbon sample, 4 carbon weights are used. Start the test with weights of 0,4; 0,5; 0,6; and 0,7 g. One of these weights should absorb 90% or more of the phenol in the test phenol solution. If the weights do not give the correct absorption adjust the weights by using higher or lower weights.
5. Weigh each carbon dose into an Erlenmeyer flask.

6. Pipette 200 mL of phenol test solution (200 mg/L phenol) into flask, using 100 mL to wet the carbon first and then rinse the sides of the flask with the remaining 100 mL.
7. Stopper flasks with rubber caps and place on a shaker at ambient temperature for 30 minutes.
8. Gravity filter the samples through a Whatman 2V, 24 cm diameter filter paper. Allow samples to filter completely.
9. Prepare 1 500 mL of buffer solution consisting of 1 volume of 8 strength buffer and 9 volumes of distilled water.
10. This solution is used as a reference solution in the spectrophotometer and as the diluent in preparing the phenol standard.
11. Pipette or use a burette to add 4,0; 8,0; 12,0; 16,0; 20,0; and 24,0 mL stock phenol solution to each of six 200 mL capacity volumetric flasks, to give standards with concentrations of 20, 40, 60, 80, 100 and 120 mg/L phenol respectively. Make up to volume with the buffer solution mixture and mix thoroughly.
12. Set the wavelength of the spectrophotometer to 270 nm.
13. Zero the spectrophotometer using the buffer solution mixture.
14. Use quartz cells and measure the absorbance of the samples and the standards.
15. For the phenol reference curve, plot mg/L phenol versus absorbance.
16. Determine the residual phenol concentration for each activated carbon treated filtrate from the phenol reference curve.

9. Calculation

Determine % residual filtrate concentration (remaining phenol) in each activated carbon treated filtrate:

$$\% \text{ Residual filtrate concentration} = \frac{\text{Residual phenol (mg/L)} \times 100}{200 \text{ (mg/L)}}$$

Determine % of X (adsorbed phenol):

$$\% X = 100 - \% \text{ residual filtrate concentration}$$

Activated carbon dosages/200 mL phenol solution, are multiplied by 5 to obtain activated carbon dosage, M g/L

Plot % X versus M (carbon dosage) (g/L).

Read off M (carbon dosage) for X = 90.

$$\text{Phenol value} = M \text{ (at } X = 90) \times \frac{100\% - \%\ \text{moisture}}{100\%}$$

10. References

1. AWWA Standard Methods for Activated Carbon, ANSI/AWWA B600-96,1996.

PHENOL NUMBER

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

STANDARDISATION OF 0,1 N SODIUM THIOSULPHATE				
Sample	**Sample Volume**	**Dilution**	**Titre Volume**	**N $Na_2S_2O_3$**
Blank				
Titre 1				
Titre 2				
Average (- blank)				

STANDARDISATION OF PHENOL SOLUTION				
Sample	**Sample Volume**	**Dilution**	**Titre Volume**	**N Phenol**
Blank				
Titre 1				
Titre 2				
Average (- blank)				

STANDARDS	
Standard (µg/L)	**Absorbance @ 620 nm**

PHENOL VALUES				
Absorbance	**Residual Phenol mg/L**	**% X**	**M g/L**	**Phenol Number**

7.4.4 TANNIN VALUE

1. Introduction

The tannin value is defined as the concentration of activated carbon in mg/L required to reduce the standard tannic acid concentration from 20 mg/L to 2 mg/L. Like the other isotherm tests described above, this test has more value as a quality control parameter than it does for assessing an activated carbon in terms of its potential for treatment applications.

2. Scope

This method describes a procedure for the determination of the tannin value of powdered activated carbon. The tannin test can be used as an indicator of an activated carbon's ability to remove high-molecular weight impurities.

3. Interferences

4. Hazards

Dust: activated carbon is an electrical conductor and should not be allowed to accumulate near or on open electrical circuits.

5. Sample Collection and Preservation

Samples may be collected in either plastic or glass containers or packets.

6. Apparatus

1. Analytical balance.
2. Jar stirrer, preferably 6 paddles.
3. 1 L tall form round or square beakers
4. 50 mL beakers
5. Vacuum filtration apparatus
6. 0,8 µm filter
7. UV spectrophotometer with 1 cm quartz cell
8. 10 L plastic bottle

7. Reagents

1. Buffer solution

- Dry anhydrous sodium phosphate dibasic (Na_2HPO_4) at 105º C for 4 hours.
- Remove from oven and cool in desiccator.
- Heat approximately 800 mL of distilled water in a 1 L beaker.
- Weigh out 133 g of dried Na_2HPO_4 and transfer to the heated water stirring continuously.
- After dissolution dilute to 12 L.
- Adjust the pH to 6,5 using concentrated phosphoric acid.

2. Tannic acid solution
   - Dry tannic acid over an indicating desiccant for 24 hours.
   - Weigh out 0,200 g of tannic acid and place in a 1 L volumetric flask, using buffer solution to transfer the tannic acid. Dissolve and make up to the mark with buffer solution.
   - Transfer the solution to a 10 L plastic bottle and add 9 L of buffer solution, mix thoroughly. **This solution must be made fresh daily and is sufficient for 2 samples**.

8. Procedure

1. Use **Table 7.1** below to determine the weight of carbon to be used in the test.

TABLE 7.1: Recommended Carbon Masses for Tannin Number Test.

Estimated Tannin Value	Recommended Isotherm Masses
	(mg carbon per 800 mL tannic acid solution)
100	60 70 85 100
200	120 145 170 200
300	180 215 250 300

2. Weigh out the unground carbon into 50 mL beakers.
3. Transfer each sample to 1 L beakers using 800 mL of tannic acid solution.
4. For a blank sample add 800 mL of tannic acid to a beaker without addition of carbon.
5. Stagger the starting times of each sample by 5 minutes.
6. Place samples, including the blank on a jar stirrer and stir at 100 rpm for 1 hour.
7. Remove the samples in the same staggered sequence from the stirrer.
8. Rinse the vacuum filtration apparatus, including the 0,8 µm filter paper for the sample, with a small portion of solution and discard.

9. Immediately vacuum filter 200 mL of sample and transfer to a clean dry beaker.
10. Continue in this manner until all 5 samples have been filtered.
11. Prepare a standard curve by diluting 10, 20, 40 and 70 mL of the original tannic acid solution into 100 mL volumetric flasks.
12. Make to the mark with buffer solution. This produces standards with 2,0; 4,0; 8,0; and 14,0 mg/L of tannic acid respectively.
13. Read the absorbance of each standard and sample at 275 nm on a UV spectrophotometer, using a 1 cm **quartz cell** and use the buffer as a reference.
14. Plot the concentration against absorbance. Prepare this curve daily.

9. Calculation

1. A data table is prepared giving the sample weight (i.e. mg/L activated carbon), mg/L tannic acid remaining and mg/L tannic acid removed. The mg/L removed per mg/L carbon (X/M) for each sample is then calculated.

2. Plot the isotherm: mg/L of original tannic acid remaining on the abscissa and total amount of tannic acid removed in mg/L per mg/L activated carbon on the ordinate using a logarithmic plot and calculate the least squares fit.

3. The effectiveness of the carbon for tannic acid removal is obtained from the plot by determining the X/M value of the carbon corresponding to 2 mg/L tannic acid residual (90% removal) and dividing it by the total amount of tannic acid removed (18 mg/L). This computed value is known as the “tannin value” of the carbon.

10. References

1. AWWA Standard Methods for Activated Carbon, ANSI/AWWA B600-96, 1996.

TANNIN VALUE

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

STANDARDS	
Standard (mg/L)	**Absorbance @ 275 nm**
2,0	
4,0	
8,0	
14,0	

DETERMINATION OF TANNIN VALUE			
Sample	**Mass Carbon (g)**	**Absorbance**	**Tannin Value**

7.4.5 MULTIPLE POINT TEST FOR GEOSMIN ADSORPTION OF PAC (UMGENI WATER METHOD)

1. Introduction

This method was developed in the Umgeni Water Research and Development Laboratories to simulate conditions on the plant as closely as possible in order to determine the effect of parameters such as contact time and treatment chemical addition. Essentially it is a modified jar test procedure and is not a true isotherm test, in that reaction is not taken to equilibrium, but is terminated before equilibrium is reached.

2. Scope

This method describes a modified jar test procedure suitable for evaluating the performance of powdered activated carbon for geosmin removal under simulated full-scale treatment conditions. It can also be used to assess PAC in terms of other treatment objectives, by changing the target contaminant.

3. Interferences

4. Hazards

Dust: activated carbon is an electrical conductor and should not be allowed to accumulate near or on open electrical circuits.

5. Sample Collection and Preservation

Collect a 25 L raw water sample in a plastic drum.

6. Apparatus

1. 6 Paddle jar stirrer
2. 1 L beakers
3. Funnels
4. Rundfilter M&N 614 24 cm filter paper (Whatman No.1 equivalent)

7. Reagents

1. Carbon slurry
    - Weigh out 0,8 g of powdered activated carbon into a beaker.
    - Transfer to a 1 L beaker and add 1 L of tap water, place on a magnetic stirrer and stir.
2. Coagulant solution
    - If using a polymeric organic coagulant, weigh out 0,8 g of coagulant solution into a beaker.
    - Transfer to a 1 L volumetric flask and dilute to the mark using tap water. May be stored for 1 week. 1 mL of this solution, when added to 800 mL water, corresponds to a coagulant addition of 1 mg/L.
    - For inorganic coagulants, such as aluminium sulphate and ferric salt solutions, weigh out 0,8 g active ingredient and dilute to 1 L as described above. For higher concentrations, use 1,6 g/L or correspondingly higher masses. 1 mL of solution, when added to 800 mL water sample corresponds to a coagulant addition of 1 mg/L and 2 mg/L for the 0,8 g/L and 1,6 g/L solutions respectively.
3. Lime solution
    - Weigh out 0,8 g of lime brown or white.
    - Transfer to a 1 L volumetric flask and dilute to the mark. May be stored for 1 week.
4. Geosmin

8. Procedure

1. Obtain operating conditions of the plant from which the raw water is collected.
2. Measure out 800 mL aliquots of raw water into 6 beakers and number them 1-6.
3. Add 200 ng/L of geosmin (or a concentration representative of that in the raw water) to all the beakers. If the raw water already contains geosmin, then addition of this contaminant may not be necessary.
4. Add carbon to beakers 2 to 6 in increments of 3 mg/L e.g. 3 mg/L, 6 mg/L, 9 mg/L, 12 mg/L and 15 mg/L (or any other appropriate increment).
5. Beaker 1 is the blank.
6. Stir at 40 rpm for 20 min. (The order and time for which the coagulant and lime are added will depend on the design of the plant.)
7. Add lime and stir at 300 rpm for 3 seconds.
8. Add coagulant and stir at 300 rpm for 2 minutes.

9. Slow mix at 40 rpm for 2 hours. This is the plant retention time in the clarifers or pulsators and can be changed to better represent the plant in question.
10. Filter the samples through Rundfilter M&N 614, 24 cm filter paper into clean 1 L glass bottles.
11. Extract the geosmin using solid phase extraction technique and analyse on the gas chromatograph/mass spectrometer.
12. If not extracted that same day, store in fridge.
13. Solid phase extraction technique
14. Using a solid phase extraction manifold pass 5 mL of methanol through, ensuring that the methanol level does not drop below the top of the cartridge packing. No vacuum is required.
15. Add 15 mL of ultra pure water to the cartridge and elute under low vacuum, again ensuring that the cartridge does not dry out.
16. The sample is passed through the cartridges at a flow rate of about 3 mL/min.
17. Once the entire sample has been passed through the cartridge, allow it to dry for 30 minutes under low vacuum.
18. Elute the analyte with 1 mL of methylene chloride into chromatographic vials.
19. Analyse geosmin using gas chromatography/mass spectrometry.

20. Parameters for Hewlett-Packard 6890/5973MSD appear in **Table 7.2**.

TABLE 7.2: GC/MS Operating Conditions for Geosmin Analysis (Umgeni Water).

	GC/MS OPERATING CONDITIONS
GC column	DB –5MS non polar
Injection Size	1,0µl
Injection mode	Splitless
Carrier Gas	Ultra high purity helium
Column program	70º C for 2 min, ramp 20º C/min to 270º C
Injector temp	250º C

10. References

1. Umgeni Water, Process Services Research and Development for the multi point isotherm.
2. Umgeni Water, Analytical Services for Solid phase extraction and GC/MS method.

7.4.6 MULTIPLE POINT TEST FOR GEOSMIN ADSORPTION OF PAC (RAND WATER METHOD)

1. Introduction

This method was developed by Rand Water and like the method described in Section 7.4.5, simulates full-scale plant conditions. This test is also essentially a modified jar test procedure and like the test described in Section 7.4.5, is not a true isotherm test in that reactions are not allowed to proceed to equilibrium.

2. Scope

This method describes a modified jar test procedure suitable for evaluating the performance of powdered activated carbon for geosmin removal under simulated full-scale treatment conditions. It can also be used to assess PAC in terms of other treatment objectives, by changing the target contaminant.

3. Interferences

4. Hazards

Dust: activated carbon is an electrical conductor and should not be allowed to accumulate near or on open electrical circuits.

5. Sample Collection and Preservation

Collect a 25 L raw water sample in a plastic drum.

6. Apparatus

1. 1 L volumetric flask
2. 6 Paddle jar stirrer
3. 1 L square beakers
4. Funnels
5. Whatman GF/C filter paper, baked at 525° C for 4 hours, cooled in a desiccator
6. 1 L Schott bottles

7. Reagents

1. Carbon slurry
    - Weigh out 100 mg of powdered activated carbon into a beaker.
    - Transfer to a 1 L volumetric flask and dilute to the mark with distilled water.
    - Place on a magnetic stirrer and stir.
2. Activated sodium silicate
    - Weigh out 1,2 g of coagulant solution as supplied into a beaker.
    - Transfer to a 1 L volumetric flask and dilute to the mark using distilled water. 1 mL of this solution, when added to 1,2 L water, corresponds to a coagulant addition of 1 mg/L.
3. Slaked lime solution
    - Weigh out 1,2 g of lime brown or white.
    - Transfer to a 1 L volumetric flask and dilute to the mark. May be stored for 1 week.

8. Procedure

1. Obtain operating conditions of the plant from which the raw water is collected.
2. Fill 6 1 L square beakers with 1,2 L of raw water.
3. Mix water for 30 seconds at 300 rpm prior to the addition of any chemicals.
4. Dose raw water at required PAC dosage using the 100 mg/L PAC solutions, while continuing to mix at 300 rpm.
5. Activated sodium silicate is then added at the required dose and then 15 seconds after this, add the required dose of slaked lime. (Activated sodium silicate and slaked lime are used as coagulants in the standard treatment process at Rand Water)
6. Mixing at 300 rpm continues for 30 seconds after the addition of the slaked lime.
7. The mixing speed is then reduced to 200 rpm and mixing continues at this speed for a further 30 seconds.
8. The mixing speed is then reduced from 200 to 60 rpm over a period of 30 seconds and mixing at 60 rpm continues at this speed for a further 420 seconds (7 minutes).
9. The mixing speed is then reduced to 30 rpm and mixing continued for a further 90 seconds, after which the stirrer is switched off and the water allowed to settle for a period of 15 minutes.
10. The supernatant is filtered through the Whatman GF/C filters and collected in 1 L Schott bottles, filled to the rim and covered in tin foil before screwing on the cap.

11. Samples are then submitted for geosmin analysis using gas chromatography/mass spectrometry.
12. The data is then fitted to a Freundlich isotherm plot in which the mg/L of geosmin remaining is the abscissa and the total amount of geosmin removed in mg/L per mg/L activated carbon is the ordinate using a logarithmic plot. Calculate the least squares fit. This allows calculation of the amount of PAC required to remove any chosen quantity of geosmin.

10. References

1. Rand Water.

7.4.7 SINGLE POINT TEST FOR GEOSMIN ADSORPTION OF PAC (THE CITY OF CAPE TOWN METHOD)

1. Introduction

This method, like the two multi-point geosmin isotherm procedures described above, is an in-house method developed for the assessment of PAC in terms of its treatment capabilities. It is also uses a modified jar test procedure, but this test uses a single PAC dose only and not multiple PAC doses as are used in Sections 7.4.5 and 7.4.6.

2. Scope

This method describes a test procedure suitable for evaluating the performance of powdered activated carbon for geosmin removal under simulated full-scale treatment conditions, using a single PAC dose.

3. Interferences

4. Hazards

Methylene chloride

Dust: activated carbon is an electrical conductor and should not be allowed to accumulate near or on open electrical circuits.

5. Sample Collection and Preservation

Samples may be collected in either plastic or glass containers.

6. Apparatus

1. 1 L Volumetric flask
2. 6 Paddle jar stirrer
3. 1 L beakers
4. Funnels
5. Solid phase extraction manifold
6. C18 solid phase extraction cartridges

7. Reagents

1. Coagulant
2. Lime
3. Geosmin
4. PAC slurry
    - Weigh out 5 g of powdered activated carbon into a beaker.
    - Transfer to a 1 L volumetric flask and dilute to the mark with distilled water. Place on a magnetic stirrer and stir.
5. Methanol
6. Methylene chloride

8. Procedure

Flocculation:

1. Spike 5 L of raw water with geosmin such that the concentration of geosmin is 200 ng/L.
2. Pour out 600 mL of the above sample and place in a beaker on a jar stirrer.
3. Set the jar stirrer to 700 rpm for 30 seconds and add the coagulant and lime dose in concentrations that correspond to the plant.
4. Add 2,4 mL of 20 mg/L PAC.
5. Stir at 30 rpm for 30 minutes and thereafter allow to settle for 30 minutes.
6. Siphon off 500 mL aliquots. Be careful not to allow the floc and PAC to carry over.
7. Run a blank solution simultaneously with the only difference being the exclusion of any addition of PAC.

Solid Phase Extraction

8. Prepare cartridge by passing through 5 mL purified water, 5 mL methanol (to activate the absorbent) followed by 2 x 5 mL purified water. (Concentration and extraction were performed using Varian Mega Bond Elut C18 solid phase extraction cartridges).
9. Wash the 500 mL of siphoned sample through the cartridge under vacuum using a solid phase extraction vacuum manifold.
10. Air dry the cartridges under vacuum for 1 hour.
11. Elute the sample by washing the cartridge with 2 mL of methylene chloride under low vacuum.
12. Transfer the isolates to chromatographic vials and make up the mass to 2,000 g with methylene chloride.

13. Analyse for geosmin using gas chromatography/mass spectrometry.
14. Parameters for Hewlett-Packard 5890 Series 11 Plus coupled to a HP 5972A mass selective detector appear in **Table 7.3**.

TABLE 7.3: GC/MS Operating Conditions for Geosmin Analysis (the City of Cape Town).

	GC/MS OPERATING CONDITIONS
GC column	HP (crosslinked 5% Ph Me silicon) 30m x 0,25 mm ID. Film thickness 0,25 µm, phase ratio 250.
Injection Size	1,2 µl
Injection mode	250º C splitting. Split flow 51 mL/min. Split ratio 54,7
Carrier Gas	Ultra high purity helium 35 cm/s linear velocity
Column program	50º C for 1 min, ramp 1:10º C/min to 180º C ramp 2:40º C/min to 275º C
Interface oven	280º C
Transfer line	280º C
Ionisation Source	195º C
Scan program	Mode:SIM (Selective Ion Monitoing) Mz = 112.10 amu

9. Calculation

The amount of geosmin removed at 20 mg/L PAC is compared for different PAC samples.

10. References

1. City of Cape Town

GEOSMIN ADSORPTION TESTS

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

GEOSMIN ADSORPTION VALUES				
Carbon mg/L	**Geosmin ng/L**	**Lime mg/L**	**Coagulant mg/L**	**Geosmin Remaining ng/L**

7.4.8 TOTAL ASH CONTENT FOR ACTIVATED CARBON

1. Introduction

The ash content of a PAC constitutes inactive material that does not have any adsorption capacity. Therefore the amount of ash present in PAC should be limited. High ash content is often an indication of a low grade carbon, but if a carbon performs well in the jar test-type tests, then the ash content is less important. Limits imposed on the ash content of a PAC are agreed upon between the supplier and the client.

2. Scope

This method describes a procedure for the determination of total ash content for activated carbon.

3. Interferences

4. Hazards

Dust: activated carbon is an electrical conductor and should not be allowed to accumulate near or on open electrical circuits.

5. Sample Collection and Preservation

Samples may be collected in either plastic or glass containers or packets.

6. Apparatus

1. Analytical balance.
2. Muffle furnace capable of reaching 650º C
3. Desiccator
4. Silica or platinum crucibles (e.g. 30 mL tall form silica crucibles without lids)
5. Oven with forced air circulation

7. Reagents

None

8. Procedure

1. Place the crucibles in the muffle furnace at 650º C for 1 hour.

2. Remove and cool to room temperature in a desiccator. Weigh crucible (M1)
3. Dry the activated carbon at 150º C for approximately 3 hours.
4. Remove and cool to room temperature in a desiccator.
5. Weigh out approximately 1 g of activated carbon into the dried, cooled silica crucible (M2).
6. Place in the muffle furnace at 650º C.
7. Ashing will require from 3 to 16 hours depending on the size and type of activated carbon.
8. Ashing is considered complete when a constant weight is achieved.
9. Place the crucible into a desiccator and allow to cool to room temperature.
10. Weigh, record weight. (M3)

9. Calculation

$$\text{Total ash content \%} = \frac{M3 - M1}{M2 - M1} \times 100$$

10. References

1. ASTM D2866 -83

7.4.9 MOISTURE IN ACTIVATED CARBON

1. Introduction

The moisture content of activated carbon is often required to define and express its properties in relation to the net weight of the carbon. High moisture content can be an indication that the carbon has been poorly stored and has adsorbed moisture from the atmosphere.

2. Scope

This method describes a procedure for the determination of moisture content for activated carbon.

3. Interferences

Heat, as some activated carbons can ignite spontaneously at temperatures as low as 150º C.

4. Hazards

Dust: activated carbon is an electrical conductor and should not be allowed to accumulate near or on open electrical circuits.

5. Sample Collection and Preservation

Samples may be collected in either plastic or glass containers or packets.

6. Apparatus

1. Analytical balance.
2. Desiccator
3. Crucibles
4. Oven with forced air circulation capable of temperature regulation between 145 and 155º C

7. Reagents

None

8. Procedure

1. Dry crucible at 150º C, cool in a desiccator and weigh (M1)
2. For PAC take a 1 to 2 g representative sample and for GAC take a 5 to 10 g representative sample, place in the pre-weighed crucible and weigh accurately to at least the nearest 0,5 mg, but preferably to four decimal points of a gram (M2).
3. Place in the pre-heated forced circulation over (at 150° C) and dry to constant weight (3 hours is usually adequate).
4. Remove crucible and dried carbon from the oven, place in a desiccator and allow to cool to room temperature.
5. Weigh, record weight (M3).

9. Calculation

$$\text{Total ash content \%} = \frac{M3 - M1}{M2 - M1} \times 100$$

10. References

1. ASTM D2866 -83

7.4.10 APPARENT DENSITY OF POWDERED ACTIVATED CARBON

1. Introduction

The apparent density of an activated carbon is the weight in grams per cubic centimetre (g/cm^3) of the carbon in air. Activated carbons should have a density which is determined at point of delivery, with corrections made for moisture content.

2. Scope

This test allows for determination of the apparent density of a powdered activated carbon in grams per cubic centimetre.

3. Interferences

4. Hazards

Dust: activated carbon is an electrical conductor and should not be allowed to accumulate near or on open electrical circuits

5. Sample Collection and Preservation

Samples may be collected in either plastic or glass containers or packets.

6. Apparatus

1. Analytical balance.
2. 100 mL graduated measuring cylinder.

7. Reagents

None

8. Procedure

1. Accurately weigh 10 g of the activated carbon to be tested.
2. Carefully transfer one third of the weighed sample to a 50 mL or 100 mL measuring cylinder.
3. While gently tamping the measuring cylinder on a rubber pad or soft surface, continue adding more activated carbon until the entire sample is transferred.

4. Tamp carbon for 5 minutes, and then continue to tamp for 2 minute periods until there is no further settling produced by a 2 minute period of tamping.
5. Record the volume of the settled activated carbon.

9. Calculation

Calculate the apparent density, in grams per cubic centimetre (g/cm^3), on the dry basis.

$$\text{Apparent density} = \frac{(\text{weight of sample}) \times (100 - \%\ \text{moisture})}{\text{volume of sample} \times 100}$$

10. References

1. AWWA Standard for Powdered Activated Carbon, ANSI/AWWA B600-96, 1996.

7.4.11 PARTICLE SIZE DISTRIBUTION

1. Introduction

Particle size distribution of a GAC is important in that it affects the flow characteristics, the adsorption kinetics and the catalytic behaviour of the carbon layers. It is also an important property in evaluating PAC, since the particle size distribution influences the settling rate of the carbon and can cause treatment problems if it does not meet the required specifications. The AWWA Standard for Powdered Activated Carbon (ANSI/AWWA B600-96) states that, unless otherwise stated by the purchaser, not less than 99% of the PAC shall pass a 150 µm (No. 100) sieve, not less than 95% shall pass through a 75 µm (No. 200) sieve and not less than 90% shall pass through a 50 µm (No. 325) sieve. The ASTM Standard Test Method for Particle Distribution of Granular Activated Carbon D 2865 – 82 (Reapproved 1987) defines GAC as a minimum of 90% retained on a 180 µm sieve. Particle size of carbons is generally determined by sieving and although standards such as those mentioned above can be found, it is the purchaser's prerogatives to modify the particle size distribution list as required. For example, a coarser-ground material may be preferred in order to prevent filter penetration by the carbon.

2. Scope

The particle size distribution of powdered and granular activated carbon is determined. For PAC an ANSI/AWWA dry sieving method is described, as well as a wet sieving method which can be used when the dry sieving procedure fail, which usually occurs if about 50% of the particles are smaller than 10 µm. A dry sieving ASTM method is described for GAC.

3. Interferences

4. Hazards

Dust: activated carbon is an electrical conductor and should not be allowed to accumulate near or on open electrical circuits

5. Sample Collection and Preservation

Samples may be collected in either plastic or glass containers or packets.

6. Apparatus

1. Analytical balance.
2. Sieves 150 µm, 75µm, 50µm for PAC.
3. Set of sieves according to the ASTM E11 Specification for Wire-Cloth Sieves for Testing Purposes for GAC.
4. 1 L Beakers
5. Large white porcelain dish
6. Shaker

7. Reagents

None

8. Procedure

1. Mix gross sample thoroughly by passing through a riffle type sample splitter and recombining twice. Then pass the mixed sample through the riffle so as to obtain a test sample of approximately 100 g. Repeat to obtain a second and third sample. If the apparent density of the carbon is less than 400 g/L, then use approximately 200 mL of sample to prevent sieve overloading and binding.
2. Accurately weigh each activated carbon and place each into a tared glass beaker.
3. Dry at 140º C for 2 h, then cool in a desiccator and weigh rapidly. This determines the drying loss and provides a record of the moisture content of the activated carbon.

Dry sieving procedure for PAC and GAC.

4. Stack sieves to be used on the bottom receiver pan, in order of increasing sieve opening from bottom to top. (use 150 µm, 75 µm and 50 µm for PAC and E11 specification sieves for GAC)
5. Place dried and weighed sample on top sieve (largest aperture sieve) and cover.
6. Place stack of sieves on shaker and shake for 10 minutes. Use with the hammer operating if the shaker has this feature, otherwise, after taking off the shaker, knock the sides of the sieves with a mallet for 5 minutes.
7. Repeat with the second and third samples.

8. Determine quantitatively the weight of carbon retained on each sieve to at least the nearest 0,1 g, but preferably to 4 decimal points of a gram.
9. Repeat for the second and third samples.

Wet Sieving Method for PAC

10. Place the weighed dry sample in a beaker and add 600 mL to 700 mL of water.
11. Wet the activated carbon thoroughly and then assemble the sieves on the bottom receiver pan with the 50 µm sieve at the bottom, 75 µm sieve in the middle and the 150 µm sieve on top.
12. Wet the sieves thoroughly and then slowly pour the mixture of activated carbon and water on the sieves, taking care not to plug them. Stir the activated carbon and the water once or twice while pouring. Wash all of the activated carbon from the beaker.
13. After all of the activated carbon has been deposited onto the sieves, wash it with a small stream of water until no activated carbon passes through the sieves.
14. Separate the sieves gently and place the 150 µm sieve over a large white porcelain dish and, while washing it with a small stream of water, collect the water passing through the sieve.
15. If additional activated carbon continues to pass, it can be seen against the white surface of the dish.
16. Wash the activated carbon that passes through the 150 µm sieve and is retained in the porcelain dish into the 75 µm sieve.
17. Continue in the same manner using the 75 µm and 50 µm sieves.
18. Using a stream of water from a small hose, transfer the activated carbon from each sieve to tared glass beakers. Dry the beakers and activated carbon at 140º C for 2 h, then cool in a desiccator and weigh.
19. Repeat with the second and third samples.
20. The net weight of activated carbon in each crucible, representing the dry weight of activated carbon from each sieve, is recorded.

9. Calculation

1. Calculate the particle size distribution from the sieve fraction weights and the sum of the fraction weights.
2. The data can be graphically represented by plotting the cumulative weight percentage passing through each sieve on the abscissa and the sieve aperture on the ordinate of using a log/probability plot.

10. References

1. AWWA Standard for Powdered Activated Carbon, ANSI/AWWA B600-96, 1996.
2. ASTM Standard Test Method for Particle Size Distribution of Granular Activated Carbon, D 2856 – 82 (Reapproved 1987).
3. ASTM Standard Specification for Wire Cloths and Sieves for Testing Purposes,E11 – 95.

ACTIVATED CARBON

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

ASH CONTENT				
Sample	**M1**	**M2**	**M3**	**% Ash**

MOISTURE CONTENT				
Sample	**M1**	**M2**	**M3**	**% Moisture**

APPARENT DENSITY			
Sample	**Mass Carbon (g)**	**Volume**	**Density (g/cm^3)**

PARTICLE SIZE DISTRIBUTION: DRY METHOD				
Sieve size	**Sieve (g)**	**Sample (g)**	**% Retained**	**% Passing**
150				
75				
50				
Pan				
PARTICLE SIZE DISTRIBUTION: WET METHOD				
Sieve size	**Beaker (g)**	**Beaker + carbon (g)**	**% Retained**	**% Passing**
150				
75				
50				
Pan				

7.4.12 THRESHOLD ODOUR TEST USING POWDERED ACTIVATED CARBON

1. Introduction

The threshold odour test is useful in determining the cost effectiveness of different types of activated carbon for removing taste and odour causing compounds from a particular water source. It can also be used in conjunction with the multiple- and single point tests described in Sections 7.4.5, 7.4.6 and 7.4.7 for the detection of geosmin and other odour-causing compounds, instead of using sophisticated gas chromatography/mass spectrometry analysis for the determination of these contaminants.

2. Scope

The threshold point is the dilution of the test water with odour-free water at the point at which the odour is just detectable. The results are reported as the threshold number, which is equal to 100 divided by the percentage of the sample in the diluted portion at the threshold point. The threshold odour test may be used to determine the activated carbon's performance in removing tastes and odours from a particular water. This test can be used to determine the optimum dose of the activated carbon needed for the removal of taste and odour compounds at a particular treatment facility.

3. Interferences

1. Smoking and eating before the test should be avoided.
2. The room in which the test is conducted should be odour free.
3. All glassware and water used for the test must be odour free.

4. Hazards

Dust: activated carbon is an electrical conductor and should not be allowed to accumulate near or on open electrical circuits

5. Sample Collection and Preservation

Collect raw water in 1 L glass bottles.

6. Apparatus

1. 500 mL Erlenmeyer flasks with ground glass stoppers
2. Thermometers two with ranges -20º C to 100º C
3. Measuring cylinders 200, 100, 50 and 25 mL
4. 10 mL Pipette
5. Hot plate
6. Carbon filter tube (five 36 mm internal diameter (ID) Corning No.9840, Kimbel No. 46170 or equivalent).
7. Whatman no 1 or equivalent.
8. 6 paddle jar stirrer capable of 200 rpm
9. Glass wool

7. Reagents

1. Carbon slurry
   - Weigh out 0,8 g of powdered activated carbon (as received) into a beaker.
   - Transfer to a 1 L beaker and add 1 L of tap water, place on a magnetic stirrer and stir. The concentration of the above solution (800 mg/L) is such that 1 mL of carbon solution will be equivalent to a dosage of 1 mg/L (ppm) in 800 mL of sample.

8. Procedure

1. Preliminary trials will be required to determine the range within which the activated carbon is to be applied. Generally, a threshold odour of about 15 requires 2 to 8 mg/L of activated carbon. The treatment applied must be such that an appreciable odour remains in some of the treated samples. The volume of each sample should be 800 mL. The stock carbon suspension should be stirred continuously at approximately 200 rpm, while it is being measured into the jars.
2. The stirring time of the samples or the contact time of the activated carbon should be the same for all samples evaluated. If known, the time of contact with the water in treatment plant practice is a good contact period to use. Otherwise, use a 1-hour contact time. At the end of the contact time, filter the samples quickly to obtain threshold values and conclusions as soon as possible. If at the treatment plant other chemicals are added at the same time as the activated carbon is applied, these chemicals, in amounts equivalent to those used in the plant should be added to the sample under examination in the same sequence as used on the plant.

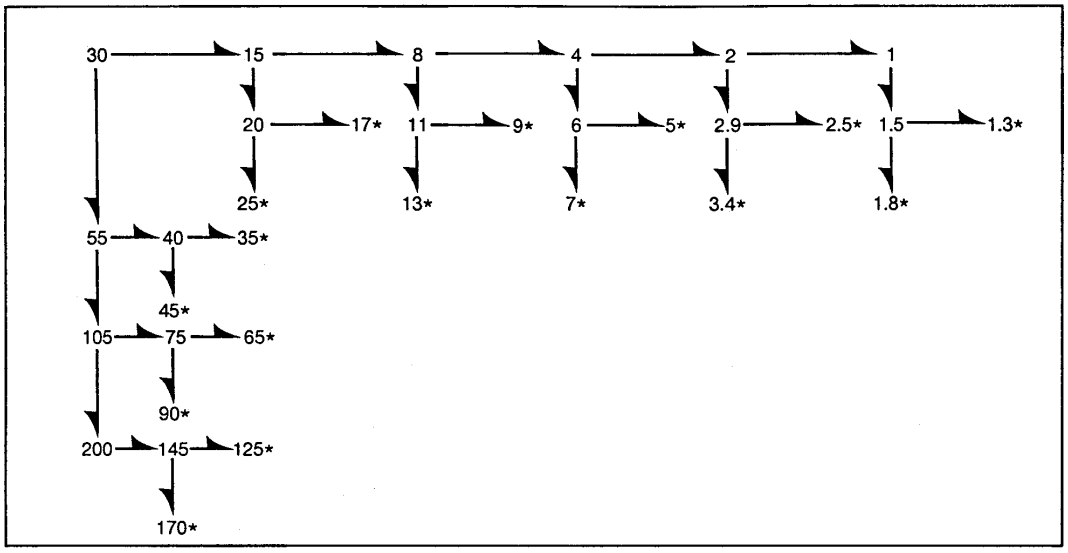
3. Place about 4 g of glass wool in each funnel and press firmly into place. Place the funnels over separate conical flasks. Wash the glass wool with odour free water until the filtrate is odour free. Filter the sample through the funnels using a separate clean funnel for each sample. Discard the first 100 mL. Collect 600 mL of the filtrated sample for the odour test.
4. This procedure includes the use of incremental differences of 15% dilution (see the Parallel threshold dilution chart in **Figure 7.2**) and requires two operators. Known as the "short parallel method," it requires a diluter and an observer to achieve the greatest precision. Using this procedure up to, five different samples can be compared simultaneously. The five samples will provide for two dosages of two different activated carbons, plus a blank consisting of raw water or raw water plus chemicals that may be added during the test, in addition to the activated carbon. Before starting the test, prepare an adequate supply (4 L) of hot (60º C to 65º C), odour free water. During the test, ensure that an adequate supply of hot odour free water is always available.
5. The diluter should label the water samples to be tested an A, B, C and so forth. The diluter should prepare a dilution by adding 30 mL of sample A to 170 mL of odour free water (200 mL total) into a flask. To another flask, add 200 mL of hot odour free water (control). Bring both flasks to 60º C and give them, without identifying them, to the observer.
6. On receiving a pair of flasks from the diluter, the observer should agitate the flasks in turn, remove the stoppers, and sniff the vapours to detect any odour. If in doubt, the observer may sniff the vapours again for confirmation. The observer should report reactions to the diluter as "positive" if odour is detected and "negative" if no odour is detected. When irregular results occur, the diluter should prepare additional check dilutions to determine threshold odour level. After the observer's reaction is noted, the flasks should be emptied, rinsed free of odour with odour free water, and returned to the diluter. The diluter should then prepare a similar dilution for each sample. After noting the observer's reaction to the first dilution of the samples tested, the diluter should refer to the parallel threshold dilution chart for further dilution (**Figure 7.2**). In every case, sufficient hot, odour-free water must be added to give a total volume of 200 mL. Response to the first dilution indicates the direction down if negative and right if positive in which the next dilution will be found on the chart. The diluter should continue to give the observer a pair of flasks; one containing only odour free water, until a response opposite to that of those already obtained is encountered with each sample.

7. After this only two more dilutions will be necessary, unless an additional confirming dilution is needed. The results for each sample tested should include at least two positive and two negative responses. If there is only one positive response, run the next highest concentration not yet tested. If only one negative response is received, then run the next lowest concentration not yet tested. The diluter should closely watch the results reported by the observer so that necessary confirming dilutions can be prepared without interrupting the continuity of the procedure. For each sample tested, the dilution containing the smallest volume of odour bearing samples in which an odour was detected determines the threshold number. Refer to the parallel threshold chart (**Table 7.4**).

TABLE 7.4: Parallel Threshold Chart

Sample volume mL	Threshold Number	Sample volume mL	Threshold Number	Sample volume mL	Threshold Number
200	1,0	35	6	6.0	35
170	1,2	30	7	5.0	40
145	1,4	25	8	4.0	50
125	1,6	20	10	3.4	60
105	1,9	17	12	2.9	70
90	2,2	15	13	2.5	80
75	2,7	13	15	2.0	100
65	3,0	11	18	1.8	110
55	3,5	9	22	1.5	135
45	4,5	8	25	1.3	150
40	5,0	7	30	1.0	200

FIGURE 7.2: Parallel Threshold Dilution Chart.



Note: the dilutions shown are in 15% increments. The numbers along the top and the left side of the figure represent every fourth possible dilution, with 30 as a starting point. When odour is positive, follow the arrow right for the next dilution. When odour is negative, follow the arrow down for the next dilution. The threshold odour is localised when a response opposite to that or to those already obtained is encountered and the immediate dilutions at that point (represented by an interior branch) are tested. The test is complete when an asterisk is reached.

10. References

1. AWWA Standard for Powdered Activated Carbon, ANSI/AWWA B600-96, 1996.

THRESHOLD ODOUR TEST

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

SHORT PARALLEL METHOD			
Sample	**Positive**	**Negative**	**Dilution**

8. FLUORIDATION CHEMICALS

8.1. INTRODUCTION

It is generally considered that a small quantity of fluorine or fluoride in drinking water (0,4 to 0,8 mg/L) promotes the formation of dental enamel and protects teeth against caries. On the other hand too much fluoride leads to the destruction of the enamel and causes a number of endemic conditions referred to collectively as fluorosis. These are dental malformation, stained tooth enamel, decalcification of bone structure, mineralisation of tendons, digestive and nervous disorders, etc. These conditions occur in different people at very different levels of fluoride content. In general however, water containing more than 1,5 mg/L of fluoride should be rejected or treated. Depending on circumstances therefore, it may be necessary either to add this element artificially or to remove it.

8.2. FLUORIDATION

This treatment comprises the addition of fluoride to water and has the approval of the WHO and is practiced mainly in the USA although cases are also quoted in Europe, Australia and South America. The process is not yet generally applied because it is not seen as being free from risk and has aroused much opposition in certain quarters.

The addition of fluoride to water is carried out using any of the following chemicals:

- Sodium hexafluorosilicate (Na_2SiF_6) is the most common
- Hexafluorosilicic acid (H_2SiF_6) or one of its salts
- Sodium fluoride (NaF)

The use of hydrofluoric acid is theoretically possible, but its extreme corrosivity renders it almost impossible to handle safely. The choice of fluoride chemical should account for factors such as the quantity that needs to be distributed what is economically available in the particular market.

Fluoridation is as yet not practiced in South Africa, although legislation enforcing its use has been published and the regulations have been issued. It is expected that

fluoride addition to water will take place at certain works in South Africa within the next 12 to 18 months. When adding fluoride to water, care should be taken that the final concentration lies close to the optimum range. In practice in this country it is expected that a fluoride concentration of 0,4 to 0,7 mg/L will be adequate and the equipment installed at a waterworks should be designed to add approximately this concentration. Care should be taken that overdosage is prevented at all costs because of the harmful consequences mentioned in the previous paragraph. The equipment used should be failsafe and should involve the use of day tanks where limited quantities of the fluoride material are transferred from the main storage tanks per day. This limits the amount of fluoride that can be added to the water in a particular period of time and is an aid to preventing overdosage. The dosage pumps should also be sized so that they normally run at close to capacity thus eliminating the possibility of setting them too high and severely overdosing the water. Fluoride chemicals are highly toxic and care is required in its handling and dosage.

The point of addition of the fluoride is not critical as it will be in solution and is not susceptible to removal in the coagulation process at the concentrations of chemicals used. It would be preferable to add it at a point where it mixes in well and any pH effects can be corrected

8.3. FLUORIDE REMOVAL

Certain natural waters can contain up to 10 mg/L of fluoride. This needs to be reduced to somewhat below 1 mg/L if the water is going to be used for potable use. A number of chemicals have been used for this purpose. Tri calcium phosphate has often been used because it is known that many natural phosphates such as apatites and phosphorites have an affinity for fluoride and always contain a substantial amount of fluorine. The same affinity applies to bones, which is why the presence of fluoride causes skeletal problems in humans. Tri calcium phosphate may be obtained from cattle bones in the form of bone char, from powdered bone, or from synthetic apatite that can be produced in water by the mixing of lime and phosphoric acid. Aluminium sulphate or alumina can also be used for fluoride removal. Alumimium sulphate is used at very large dosages ranging from 150 to over 1 000 mg/L according to circumstances. Activated alumina is often used as a filter material and can be regenerated by aluminium sulphate or caustic soda and sulfuric acid. The removal capacity of activated alumina may vary between 0,3 and 4,4g of fluoride per

litre of product. Lime softening of water can also be used to remove fluoride provided it has sufficient magnesium content. About 50 mg/L of magnesium is required to remove 1 mg/L of fluoride.

With the recent development of membrane processes, these are also an option for fluoride removal. Obviously a fine pore membrane is required in the reverse osmosis (RO) range if ions are to be removed. The process is not selective however and other ions such as chloride and sulphate will be removed as well. This may lead to a need to reintroduce desirable ions depending on the relative concentrations.

From the processes outlined above it can be seen that fluoride removal requires either a settling or a filtration stage or both. For industrial purposes settling may be sufficient, but if the water is to be used for potable purposes the filtration process provides a more positive barrier.

8.4. EVALUATION OF FLUORIDE

The most important aspect in selection of a fluoride chemical is the concentration of the active ingredient (fluoride). Obviously the presence of contaminants that might be deleterious to the health of those consuming the water, are undesirable and it should be ensured that levels of arsenic, lead and other heavy metals fall within specified concentration ranges.

The simplest method for detecting fluoride concentration, is to use a fluoride ion-selective electrode. However, the fluoride solution must be kept away from glass, so both the electrode and all sample containers must be made of a material that is resistant to fluoride corrosion.

Another method of determining the concentration of a solution is to measure its specific gravity. This can be done either by weighing a measured volume of the solution, or by using an appropriate hydrometer, although avoid using glass or, if this is not possible, limit the time that glass equipment is in contact with the fluoride solutions. This method provides only a rough approximation of the acid content and should not be used if an exact determination of the acid is required.

Other simple titration type tests are also available for determination of factors such as the free acid present in fluosilicic acid, which can be used for quality control purposes. These are presented subsequently in this chapter.

8.5. ANALYTICAL METHODS

8.5.1. SODIUM FLUOROSILICATE AND FLUORIDE CONTENT OF SOLID SODIUM FLUOROSILCATE

1. Introduction

Sodium fluorosilicate (Na_2SiF_6) is generally supplied in solid form as a fine, dry granular material with an average bulk density of approximately 1,4 g/cm^2. According to the AWWA Standard for Sodium Fluorosilicate (ANSI/AWWA B702-94) it should contain at least 98% m/m (on a dry basis) sodium fluorosilicate, which is equivalent to 59,4% fluoride. This method provides a procedure for measuring the sodium fluorosilicate and fluoride content of solid sodium fluorosilicate.

2. Scope

This method may be used to determine the percentage sodium fluorosilicate or fluoride present in solid sodium fluorosilicate.

3. Interferences

4. Hazards

Sodium fluorosilicate

Highly corrosive: it is imperative that protective clothing is worn when handling this compound.

Ensure that you are familiar with the dangers and treatment associated with this substance.

5. Sample Collection

Sodium fluorosilicate may be sampled using a sampling tube that is at least 19 mm in diameter and should be representative of the entire delivery. Samples must be sealed in airtight and moisture-proof glass or plastic containers. Exposure of the sample to the air must be minimised at all times.

6. Apparatus

1. Weighing dish or small beaker (50 mL)

2. Balance capable of measuring to 2 decimal points of a gram.
3. 500 mL and 1 L beakers
4. 1 L volumetric flask
5. 50 mL burette
6. Measuring cylinders
7. Buchner funnel and vacuum pump/tap
8. Filter paper (Whatman No. 1 or equivalent)

7. Reagents

1. Alcoholic potassium chloride solution.
    - Dissolve 60 g potassium chloride in 400 mL of recently boiled and cooled distilled water.
    - Add 400 mL of 95% neutral ethyl alcohol to the potassium chloride solution.
2. Alcoholic potassium chloride and sodium carbonate solution.
    - Dissolve 1 g of sodium carbonate in 100 mL of the alcoholic potassium chloride solution prepared in 7.1.
3. 1,0 N Sodium hydroxide solution stock solution.
    - Weigh out 40,00 g of sodium hydroxide pellets into a plastic beaker.
    - Dissolve carefully in distilled water, as this is an exothermic reaction.
    - Transfer to a 1 L volumetric flask and dilute to the mark with distilled water.
4. 0,2 N Standard sodium hydroxide solution
    - Using the 1 N NaOH, measure 200,0 mL of the 1 N solution into a 1 000 mL volumetric flask and make to the mark using distilled water.
    - Standardise by titrating against standard potassium hydrogen phthalate solution
5. Potassium hydrogen phthalate solution (approximately 0,05 N)
    - Crush 15 to 20 g primary standard $KHC_8H_4O_4$ to about 150 µm (100 mesh) and dry at 120° C for 2 hours.
    - Cool in a desiccator.
    - Weigh 10,0 ± 0,5 g (to the nearest mg), transfer into a 1 L volumetric flask and dilute to the mark using distilled water.
6. 1% Phenolphthalein indicator solution.
    - Dissolve 1 g phenolphthalein in a small amount of ethanol and dilute to 100 mL using distilled water.

8. Analytical Procedure

1. Standardisation of 0,2 N sodium hydroxide.
   - Titrate 50 mL of potassium hydrogen phthalate solution (approximately 0,05 N) against approximately 0,2 N sodium hydroxide using a 25 or 50 mL burette.
   - Titrate with pheolphthalein to the end point, which should be close to pH 8,7.
   - Calculate the normality of the NaOH:

$$\text{N NaOH} = \frac{\text{A x B}}{\text{204,2 x C}}$$

   Where:

   A = g $KHC_8H_4O_4$ weighed into the 1l flask

   B = mL $KHC_8H_4O_4$ solution used for the titration

   C = mL NaOH solution used
2. Weigh 0,4 g of sodium fluorosilicate sample that has been dried at 105° C to constant weight and transfer into a beaker.
3. While stirring continuously, rapidly add 25 ml alcoholic potassium chloride/sodium carbonate solution. The pH of this solution should be greater than 7 (i.e. the solution must not be acidic). If the pH is still acidic after the addition of 25 ml, add more.
4. Filter through filter paper with a Buchner funnel under suction and wash the precipitate with alcoholic potassium chloride solution until the wash liquid is not alkaline to phenolphthalein.
5. Transfer the filter paper and contents to a beaker and add 100 mL of recently boiled distilled water and 1 to 2 mL phenolphthalein indicator.
6. Heat to between 70 and 90° C and titrate with 0,02 N sodium hydroxide to first pink colour. Continue heating during this time, so that the titration is completed with the solution actively boiling.

9. Calculations

$$\%\ Na_2SiF_6 = \frac{\text{mL NaOH x N NaOH x 0,047}}{\text{weight sample (g)}} \text{ x 100}$$

$$\%\ F = \%\ Na_2SiF_6 \text{ x 0,606}$$

10. References

1. AWWA Standard for Sodium Fluorosilicate, ANSI/AWWA B702-94.
2. “Standard Methods for the Examination of Water and Wastewater”, 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.

8.5.2. SIEVE GRADING FOR SODIUM FLUOROSILICATE

1. Introduction

Sodium fluorosilicate should be a fine, dry granular material containing no lumps and having an average bulk density of 1,4 g/cm^3. According to AWWA Standard for Sodium Fluorosilicate (ANSI/AWWA B702-94) at least 98% should pass through a 420 µm sieve and less than 25% should pass through a 45 µm sieve.

2. Scope

This method describes a procedure for the determination of the size of sodium fluorosilicate powders.

3. Interferences

4. Hazards

Sodium fluorosilicate.

Highly corrosive: it is imperative that protective clothing is worn when handling this compound.

Ensure that you are familiar with the dangers and treatment associated with this substance.

5. Sample Collection and Preservation

Sodium fluorosilicate may be sampled using a sampling tube that is at least 19mm in diameter and should be representative of the entire delivery. Samples must be sealed in airtight and moisture-proof glass or plastic containers. Exposure of the sample to the air must be minimised at all times.

6. Apparatus

1. Analytical balance.
2. Weighing dish or beaker.
3. Sieves of pore size 420 µm and 45 µm.

7. Reagents

None

8. Analytical Procedure

1. Record the mass of the empty weighing dish or beaker and of the two sieves.
2. Weigh out 100,0 g of sample to the nearest 0,1 g.
3. Stack sieves on the bottom receiver pan with the 45 µm sieve at the bottom and the 420 µm sieve at the top.
4. Transfer weighed sample onto 420 µm sieve and cover.
5. Screen sample until both sieves reach constant weight.
6. Weigh sieves (or residue retained on each sieve) or material passing through each sieve to the nearest 0,01 g.
7. Report each portion passing through the sieves or retained on the sieves as a percentage of the total initial sample.
8. The test should be conducted in a dry atmosphere and should be completed as quickly as possible

9. Calculation of Results

$$\% \text{ Retained material} = \frac{(M2 - M1) \times 100}{100}$$

Where:

M1 = mass of empty sieve (g).

M2 = mass of sieve plus residue retained (g).

OR:

$$\% \text{ Material passing through} = \frac{100 - (M2 - M1)}{100} \times 100$$

Where:

M1 = mass of empty sieve (g).

M2 = mass of sieve plus residue retained (g).

10. References

1. AWWA Standard for Sodium Fluorosilicate, ANSI/AWWA B702-94.

8.5.3. INSOLUBLE MATTER IN SODIUM FLUOROSILICATE

1. Introduction

Sodium fluorosilicate should contain at least 98% (dry basis) sodium fluorosilicate or approximately 59,4% fluoride ions according to the AWWA Standard for Sodium Fluorosilicate (ANSI/AWWA B702-94) and the insoluble matter present in a sample of sodium fluorosilicate should not exceed 0,5%.

2. Scope

This method describes a procedure for the determination of insoluble matter present in sodium fluorosilicate.

3. Interferences

4. Hazards

Sodium fluorosilcate.

Highly corrosive: it is imperative that protective clothing is worn when handling this compound.

Ensure that you are familiar with the dangers and treatment associated with this substance.

5. Sample Collection and Preservation

Sodium fluorosilicate may be sampled using a sampling tube that is at least 19 mm in diameter and should be representative of the entire delivery. Samples must be sealed in airtight and moisture-proof glass or plastic containers. Exposure of the sample to the air must be minimised at all times.

6. Apparatus

1. Analytical balance.
2. Oven at 105° C.
3. Desiccator
4. 1 L beaker
5. Gooch crucibles or fritted-glass filter of medium porosity

7. Reagents

None

8. Procedure

1. Weigh 2 g of the sample that has been previously dried at 105° C to constant weight and transfer into a beaker.
2. Dissolve in 500 mL hot distilled water (between 15 and 30 minutes is generally adequate).
3. Filter through a tared Gooch crucible or fritted-glass filter.
4. Wash with at least six separate 25 mL portions of boiling distilled water, allowing the crucible or filter to drain between washings.
5. Dry the crucible or filter at 105° C to constant weight.

9. Calculation

$$\% \text{ Insoluble matter} = \frac{M2}{M1} \times 100$$

Where:

M1 = mass of sample (g).

M2 = mass of residue (g).

10. References

1. AWWA Standard for Sodium Fluorosilicate, ANSI/AWWA B702-94

8.5.4. MOISTURE IN SODIUM FLUOROSILICATE

1. Introduction

According to the AWWA Standard for Sodium Fluorosilicate (ANSI/AWWA B702-94) the moisture content should not exceed 0,5% by weight. Caution should be exercised when sampling sodium fluorosilicate to avoid changes in moisture content and samples should be stored in airtight containers, which are only unsealed for sample extraction and then resealed immediately afterwards.

2. Scope

This method describes a procedure for the determination of moisture content in sodium fluorosilicate.

3. Interferences

4. Hazards

Sodium fluorosilcate.

Highly corrosive: it is imperative that protective clothing is worn when handling this compound.

Ensure that you are familiar with the dangers and treatment associated with this substance.

5. Sample Collection and Preservation

Sodium fluorosilicate may be sampled using a sampling tube that is at least 19 mm in diameter and should be representative of the entire delivery. Samples must be sealed in airtight and moisture-proof glass or plastic containers. Exposure of the sample to the air must be minimised at all times.

6. Apparatus

1. Analytical balance.
2. Desiccator
3. Broad weighing bottle
4. Oven at 105° C

7. Reagents

None

8. Procedure

1. Weigh 5 g of sample to the closest 0,01 g into a weighed broad weighing bottle which has been previously dried and cooled.
2. Heat in the oven at 105° C to constant weight.
3. Cool in a desiccator and reweigh.

9. Calculation

$$\% \text{ Moisture} = \frac{M2 - M3}{M2 - M1} \times 100$$

Where:

M1 = mass of weighing bottle (g).

M2 = mass of weighing bottle and sample before drying (g).

M3 = mass of weighing bottle and sample after drying (g).

10. References

1. AWWA Standard for Sodium Fluorosilicate, ANSI/AWWA B702-94

8.5.5. HEAVY METALS IN SODIUM FLUOROSILICATE

1. Introduction

Heavy metals present in sodium fluorosilicate, when expressed as lead, should not exceed 0,05% by weight, according to the AWWA Standard for Sodium Fluorosilicate (ANSI/AWWA B702-94). There are a number of methods available for the determination of heavy metals, atomic absorption being one of the more popular. However, this method provides a more simple wet chemistry procedure that can be carried out without the need for sophisticated equipment.

2. Scope

This method describes a procedure for the determination of the heavy metal content of sodium fluorosilicate.

3. Interferences

4. Hazards

1. Sodium Fluorosilcate.

   Highly corrosive: it is imperative that protective clothing is worn when handling this compound.

   Ensure that you are familiar with the dangers and treatment associated with this substance.

2. Ammonium hydroxide.

   Ammonium hydroxide fumes can cause damage to eyes and lungs. Use in well ventilated area or under a fume hood.

5. Sample Collection and Preservation

Sodium fluorosilicate may be sampled using a sampling tube that is at least 19mm in diameter and should be representative of the entire delivery. Samples must be sealed in airtight and moisture-proof glass or plastic containers. Exposure of the sample to the air must be minimised at all times.

6. Apparatus

1. Analytical balance.
2. 1 L volumetric flasks
3. 100 mL volumetric flasks
4. 100 mL beakers
5. Platinum dish
6. Fume hood

7. Reagents

1. Ammonium hydroxide, 10%
2. Hydrochloric acid, concentrated
3. Hydrochloric acid 0,1 N
    - Dissolve 8,3 mL of concentrated acid into at least 500 mL distilled water and the dilute to 1 L with distilled water. Always add concentrated acids to water and add slowly, with caution.
4. Hydrogen sulphide, saturated solution
5. Lead nitrate stock solution
    - Dissolve 400,0 mg of reagent grade lead nitrate [$Pb(NO_3)_2$] in 100 mL distilled water containing 1 mL concentrated nitric acid and dilute to 1 000 mL with distilled water.
    - Prepare and store this solution in containers that are free from lead salts.
6. Standard lead solution
    - On the day of analysis, dilute 10,0 mL of the lead nitrate stock solution to 100,0 mL with distilled water (20 mL of this solution contains 0,50 mg of lead, which is equivalent to 0,05% heavy metals in 2,0 g of sodium fluorosilicate).
7. Nitric acid, concentrated

8. Procedure

1. Place 2,0 g of sample that has been previously dried at 105° C to constant weight, in a platinum crucible.
2. Treat this sample with 10 mL concentrated hydrochloric acid.
3. Evaporate contents of platinum crucible to dryness in a fume hood.
4. Repeat the treatment with another 10 mL concentrated hydrochloric acid and again evaporate to dryness in a fume hood.
5. Dissolve the residue in 40 mL of distilled water.

6. Measure out 20 mL of this solution into a 100 mL beaker and adjust to pH 3 to 4 with 10% ammonium hydroxide or 0,1 N hydrochloric acid or both.
7. Add 10 mL of a freshly prepared saturated solution of hydrogen sulphide in distilled water and observe the brown colour formed.
8. Repeat steps 8.6 and 8.7 using 20 mL of the standard lead solution.

9. Result

The brown colour formed using the solution prepared from the sample should not be greater than that formed in the standard lead solution. If it is, then the sample fails the specification.

10. References

1. AWWA Standard for Sodium Fluorosilicate, ANSI/AWWA B702-94
2. Standard Methods for the Examination of Water and Wastewater, 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.

SODIUM FLUOROSILICATE

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

STANDARDISATION OF 0,2 N SODIUM HYDROXIDE				
Sample	**Sample Volume**	**Dilution**	**Titre Volume**	**N NaOH**
Blank				
Titre 1				
Titre 2				
Average (- blank)				

PERCENTAGE SODIUM FLUOROSILICATE			
Sample	**Mass (g)**	**Volume (mL)**	**% Na_2SiF_6**
Blank			
Titre 1			
Titre 2			
Average (- blank)			

SIEVE GRADING				
Sample	**M1 (g)**	**M2 (g)**	**% Retained**	**% Passing**
420 µm				
45 µm				

INSOLUBLE MATTER			
Sample	**M1 Sample (g)**	**M2 Residue (g)**	**% Insoluble Matter**

MOISTURE CONTENT				
Sample	**M1 (g)**	**M2 (g)**	**M3 (g)**	**% Moisture**

HEAVY METALS		
Sample	**Sample: Colour Intensity**	**Std. Lead: Colour Intensity**

8.5.6. FLUOROSILICIC ACID CONTENT USING THE HYDROGEN TITRATION METHOD

1. Introduction

Fluorosilicic acid is an aqueous solution of H_2SiF_6 and can be water white to straw yellow in colour. It is a corrosive acid with a pungent odour.

2. Scope

This method may be used to determine the percentage of fluorosilicic acid. This method utilizes the titration of ionisable hydrogen in a chilled solution from which the fluorosilicate ions have been precipitated as potassium fluorosilicate.

3. Interferences

4. Hazards

Fluorosilicic acid

Highly corrosive: it is imperative that protective clothing is worn when handling this acid.

Ensure that you are familiar with the dangers and treatment associated with this substance.

5. Sample Collection

Samples may be collected in either plastic or rubber containers. Containers that are lined with acid-resistant plastic, wax or rubber may also be used.

6. Apparatus

1. 25 mL pipette
2. 500 mL volumetric flasks
3. 400 mL beakers

7. Reagents

1. Potassium nitrate-saturated solution
2. 0,5 N sodium hydroxide solution
3. 0,2% Bromothymol blue solution

4. Deionised ice (can be made from distilled water).

8. Analytical Procedure

1. Pipette 25,0 mL of sample into a 500 mL volumetric flask.
2. Make up to mark with distilled water and mix. (If this dilution produces a precipitate, pipette a smaller sample volume in 5,0 mL increments until no precipitate forms).
3. Into a 400 mL beaker put 100 to 150 mL of clean, deionised ice.
4. Onto the ice add 25 mL of potassium nitrate solution.
5. Now pipette 25,0 mL of the diluted sample into the beaker.
6. Wash the sides of the beaker with distilled water.
7. Stirring constantly, titrate immediately against the sodium hydroxide, using bromothymol blue as the indicator.
8. The endpoint is reached when a blue colour persists for at least 30 seconds. On standing longer the indicator will turn yellow.

9. Calculations

$$\text{Volume of sample taken, mL (D)} = C \times \frac{A}{B}$$

Weight of sample (g) = D x specific gravity (at room temperature)

$$\%\ H_2SiF_6 = \frac{\text{mL NaOH x N (NaOH) x 0,072 x 100}}{\text{weight if sample (g)}}$$

Where:

A = original sample volume, in mL

B = diluted sample volume, in ml (generally 500 mL)

C = aliquot volume, mL

10. References

1. AWWA Standard for Fluorosilicic Acid, ANSI/AWWA B703-00, 2000.

8.5.7. FREE ACID CONTENT OF FLUOROSILICIC ACID

1. Introduction

This method can be used to analyse for free acids other than fluorosilicic acid, that may be present in fluorosilicic acid solutions

.

2. Scope

The hydrogen titration method includes any free acid other than fluorosilicic acid that may be present. If it is necessary to distinguish between fluorosilicic acid and other acids, use the contents of the beaker that have been titrated in the hydrogen method described in Section 8.5.6.

3. Interferences

4. Hazards

Fluorosilicic acid.

Highly corrosive: it is imperative that protective clothing is worn when handling this acid.

Ensure that you are familiar with the dangers and treatment associated with this substance.

5. Sample Collection

Samples may be collected in either plastic or rubber containers. Containers that are lined with acid-resistant plastic, wax or rubber may also be used.

6. Apparatus

1. 25 mL pipette
2. 500 mL volumetric flasks
3. 400 mL beakers

7. Reagents

1. Potassium nitrate-saturated solution
2. 0,5 N sodium hydroxide solution
3. 0,2% Bromothymol blue solution

4. Deionised ice (can be made from distilled water).

8. Analytical Procedure

1. Bring the final solution from the hydrogen titration method to the boil, by heating on a hot plate.
2. Titrate the hot solution with sodium hydroxide to the neutral point of the bromothymol blue. This titration breaks down the fluorosilicate radical of the potassium fluorosilicate.

If the fluorosilicic acid is 100 percent pure, the volume of sodium hydroxide used in the cold titration will equal exactly half the volume of sodium hydroxide of the hot titration. If free acid other than fluorosilicic is present, the cold titre will exceed half the hot titre.

If fluorosilicate salts are present, half the hot titre will exceed the cold titre.

9. Calculation

% free acid other than H_2SiF_6 , expressed as:

$$HF = \frac{\text{mL NaOH (cold)} - \frac{\text{mL NaOH (hot)}}{2} \times N\,(NaOH) \times 0{,}02 \times 100}{\text{weight sample (g)}}$$

$$\%\ H_2SiF_6 = \frac{\frac{\text{mL NaOH (hot)}}{2} \times N(NaOH) \times 0{,}072 \times 100}{\text{weight sample (g)}}$$

10. References

1. AWWA Standard for Fluorosilicic Acid, ANSI/AWWA B703-00, 2000.

8.5.8. SPECIFIC GRAVITY OF FLUOROSILICIC ACID

1. Introduction

Fluorosilicic acid (H_2SiF_6) can be used in water treatment for fluoridation of the potable water supply.

2. Scope

This method may be used to determine the percentage of fluorosilicic acid.

3. Interferences

4. Hazards

Fluorosilicic acid

Highly corrosive: it is imperative that protective clothing is worn when handling this acid.

Ensure that you are familiar with the dangers and treatment associated with the above substance.

5. Sample Collection

Samples may be collected in either plastic or rubber containers. Containers that are lined with acid-resistant plastic, wax or rubber may also be used.

6. Apparatus

Hydrometer method

1. Acid resistant plastic measuring cylinder or dish, with sufficient depth to float a hydrometer.
2. Glass hydrometer (long stem), able to read to 4 decimal places. If the density of the solution varies over a wide range three or more hydrometers will be needed.

Mass and volume method

3. Analytical balance
4. Volumetric flasks 50 mL
5. Dropper pipettes

7. Reagents

None

8. Analytical Procedure

Hydrometer Method:

1. Transfer the fluorosilicic acid into the cylinder and adjust the temperature to 17,5º C.
2. Insert the hydrometer and measure the specific gravity.
3. Record the reading.

Mass and Volume Method:

4. Place the volumetric flask without the stopper on the balance and tare it.
5. Remove the flask from the balance and take to a fume cupboard.
6. There transfer 50 mL of fluorosilicic acid solution to the volumetric flask without bringing the acid into contact with the neck of the flask.
7. Fill to the 50 mL mark and return to the balance and record the reading.
8. The fluorosilicic acid should not be left in the flask once the test has been completed as it etches glass.

9. Calculation

The percentage fluorosilicic acid can be determined from **Table 7.5** below.

Table 8.1: Specific Gravity, Degrees Baume and % Fluorosilicic Acid at 17,5° C

Specific Gravity	Degrees Baume	%H_2SiF_6	Specific Gravity	Degrees Baume	%H_2SiF_6
1,1512	19,0	17,5	1,2335	27,5	26,0
1,1559	19,6	18,0	1,2385	27,9	26,5
1,1606	20,1	18,5	1,2436	28,4	27,0
1,1653	20,6	19,0	1,2486	28,9	27,5
1,1701	21,1	19,5	1,2537	29,3	28,0
1,1748	21,6	20,0	1,2588	29,8	28,5
1,1796	22,1	20,5	1,2639	30,3	29,0
1,1844	22,6	21,0	1,2691	30,7	29,5
1,1892	23,1	21,5	1,2742	31,2	30,0
1,1941	23,6	22,0	1,2794	31,7	30,5
1,1989	24,1	22,5	1,2846	32,1	31,0
1,2038	24,6	23,0	1,2898	32,6	31,5
1,2087	25,0	23,5	1,2951	33,0	32,0
1,2136	25,5	24,0	1,3003	33,5	32,5
1,2186	26,0	24,5	1,3056	34,0	33,0
1,2235	26,5	25,0	1,3109	34,4	33,5
1,2285	27,0	25,5	1,3162	34,8	34,0

10. References

1. AWWA Standard for Fluorosilicic Acid, ANSI/AWWA B703-00, 2000.

8.5.9. HEAVY METALS IN FLUOROSILICIC ACID

1. Introduction

According to the AWWA Standard for Sodium Fluorosilicate (ANSI/AWWA B703-00) the heavy metals present in fluorosilicic acid expressed as lead, should not exceed 0,02% by weight. Heavy metals can be analysed using atomic absorption spectrometry, but it is also possible to determine the total heavy metal content using a more simple wet chemistry procedure that can be carried out without the need for sophisticated equipment. Although this method does not provide the accuracy that atomic absorption spectrometry does, it nevertheless offers an alternative means of determining whether fluorosilicic acid meets the specifications for heavy metal content.

2. Scope

This method describes a procedure for the determination of the heavy metal content of fluorosilicic acid.

3. Interferences

4. Hazards

1. Fluorosilicic acid.

   Highly corrosive: it is imperative that protective clothing is worn when handling this acid.

   Ensure that you are familiar with the dangers and treatment associated with this substance.
2. Ammonium hydroxide.

   Ammonium hydroxide fumes can cause damage to eyes and lungs. Use in well ventilated area or under a fume hood.

5. Sample Collection and Preservation

Sodium fluorosilicate may be sampled using a sampling tube that is at least 19mm in diameter and should be representative of the entire delivery. Samples must be sealed in airtight and moisture-proof glass or plastic containers. Exposure of the sample to the air must be minimised at all times.

6. Apparatus

1. Analytical balance.
2. 1 L volumetric flasks
3. 100 mL volumetric flasks
4. 100 mL beakers
5. Fume hood

7. Reagents

1. Ammonium hydroxide, 10%
2. Hydrochloric acid, concentrated
3. Hydrochloric acid 0,1 N
    - Dissolve 8,3 mL of concentrated acid into at least 500 mL distilled water and the dilute to 1 L with distilled water. Always add concentrated acids to water and add slowly, with caution.
4. Hydrogen sulphide, saturated solution
5. Lead nitrate stock solution
    - Dissolve 320,0 mg of reagent grade lead nitrate [$Pb(NO_3)_2$] in 100 mL distilled water containing 1 mL concentrated nitric acid and dilute to 1 000 mL with distilled water.
    - Prepare and store this solution in containers that are free from lead salts.
6. Standard lead solution
    - On the day of analysis, dilute 10,0 mL of the lead nitrate stock solution to 100,0ml with distilled water (20 mL of this solution contains 0,40 mg of lead, which is equivalent to 0,02% heavy metals in 4,0 g of fluorosilicic acid).
7. Nitric acid, concentrated

8. Procedure

1. Place 4,0 g of sample in a 100 mL beaker and add 40 mL distilled water.
2. Measure out 20 mL of this solution into a 100 mL beaker and adjust to pH 3 to 4 with 10% ammonium hydroxide or 0,1 N hydrochloric acid or both.
3. Add 10 mL of a freshly prepared saturated solution of hydrogen sulphide in distilled water and observe the brown colour formed.
4. Repeat steps 8.2 and 8.3 using 20 mL of the standard lead solution.

9. Result

The brown colour formed using the solution prepared from the sample should not be greater than that formed in the standard lead solution.

10. References

1. AWWA Standard for Fluorosilicic acid, ANSI/AWWA B703-00
2. Standard Methods for the Examination of Water and Wastewater, 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.

FLUOROSILICIC ACID

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

FLUOROSILICIC ACID CONTENT				
Sample	**Sample mL**	**Diluted Sample mL**	**NaOH Titre mL**	**% H_2SiF_6**

FREE ACID CONTENT		
Sample	**NaOH Titre mL**	**% HF**

SPECIFIC GRAVITY				
Sample	**M1**	**M2**	**M3**	**SG**
420 µm				
45 µm				

HEAVY METALS		
Sample	**Sample: Colour Intensity**	**Std. Lead: Colour Intensity**

8.5.10. FLUORIDE CONTENT OF SOLID SODIUM FLUORIDE

1. Introduction

Sodium fluoride (NaF) is usually supplied as a dry, coarse crystalline material and should, according to the AWWA Standard for Sodium Fluoride (ANSI/AWWA B701-94) contain at least 97% m/m (on a dry basis) sodium fluoride, which is equivalent to 44% fluoride ion.

2. Scope

This method may be used to determine the percentage sodium fluoride present in sodium fluoride.

3. Interferences

4. Hazards

Sodium fluoride

Highly corrosive: it is imperative that protective clothing is worn when handling this compound.

Ensure that you are familiar with the dangers and treatment associated with this substance.

5. Sample Collection

Sodium fluoride may be sampled using a sampling tube that is at least 19mm in diameter and should be representative of the entire delivery. Samples must be sealed in airtight and moisture-proof glass or plastic containers. Exposure of the sample to the air must be minimised at all times.

6. Apparatus

1. Mortar and pestle
2. Weighing dish or small beaker (50 mL)
3. Balance capable of measuring to 2 decimal points of a gram.
4. 250 mL beakers
5. 1 L volumetric flask
6. 500 mL beakers

7. 50 mL burette
8. Measuring cylinders
9. Buchner funnel and vacuum pump/tap or filter crucible
10. Filter paper (Whatman No. 1 or equivalent)

7. Reagents

1. Alcoholic potassium chloride solution.
    - Dissolve 60 g potassium chloride in 400 mL of recently boiled and cooled distilled water.
    - Add 400 mL of 95% neutral ethyl alcohol to the potassium chloride solution.
2. Powdered silica gel.
3. Hydrochloric acid, concentrated.
4. Methyl orange indicator, 0,5%
5. Potassium chloride crystals
6. Ethyl alcohol, neutral
7. 1,0 N Sodium hydroxide solution stock solution.
    - Weigh out 40,00 g of sodium hydroxide pellets into a plastic beaker.
    - Dissolve carefully in distilled water, as this is an exothermic reaction.
    - Transfer to a 1 L volumetric flask and dilute to the mark with distilled water.
8. 0,2 N Standard sodium hydroxide solution
    - Using the 1 N NaOH, measure 200,0 mL of the 1 N solution into a 1 000 mL volumetric flask and make to the mark using distilled water.
    - Standardise by titrating against standard potassium hydrogen phthalate solution
9. Potassium hydrogen phthalate solution (approximately 0,05 N)
    - Crush 15 to 20 g primary standard $KHC_8H_4O_4$ to about 150 µm (100 mesh) and dry at 120° C for 2 hours.
    - Cool in a desiccator.
    - Weigh 10,0 ± 0,5 g (to the nearest mg), transfer into a 1 L volumetric flask and dilute to the mark using distilled water.
10. 1% Phenolphthalein indicator solution.
    - Dissolve 1 g phenolphthalein in a small amount of ethanol and dilute to 100 mL using distilled water.

8. Analytical Procedure

1. Standardisation of 0,2 N sodium hydroxide.

- Titrate 50 mL of potassium hydrogen phthalate solution (approximately 0,05 N) against approximately 0,02 N sodium hydroxide using a 25 or 50 mL burette.
- Titrate with phenolphthalein to the end point, which should be close to pH 8,7.
- Calculate the normality of the NaOH:

$$\text{N NaOH} = \frac{\text{A x B}}{\text{204,2 x C}}$$

Where:

A = g $KHC_8H_4O_4$ weighed into the 1 L flask

B = mL $KHC_8H_4O_4$ solution used for the titration

C = mL NaOH solution used

1. Grind a sample of approximately 1 g to a powder using a mortar and pestle and then dry to constant weight at 105° C.
2. Weigh 0,5 g ground, dried sample and transfer to a 250 mL beaker.
3. Add 20 to 25 mL distilled water.
4. Add 0,5 g silica gel, a few drops of methyl orange indicator and concentrated hydrochloric acid dropwise to a permanent pink colour, and then add another 0,5 mL hydrochloric acid.
5. Bring the solution just to boiling point and then cool to room temperature.
6. Add 4,0 g of potassium chloride and stir until dissolved or place on a shaking machine for at least 30 minutes.
7. Add 25 mL of neutral ethyl alcohol and allow to stand for 1 hour.
8. Filter through filter paper with a Buchner funnel or a filter crucible under suction and wash the precipitate with alcoholic potassium chloride solution until one washing does not remove the colour made by one drop of 0,2 N sodium hydroxide and phenolphthalein indicator.
9. Transfer the filter paper and contents to a 500 mL beaker.
10. Add 200 mL of recently boiled distilled water and 1 to 2 mL of 1% phenolphthalein indicator.
11. Heat to 70 to 90° C and titrate with 0,2 N sodium hydroxide to first pink colour. Complete the titration with the solution actively boiling.

9. Calculations

$$\% \text{ NaF} = \frac{\text{mL NaOH x N NaOH x } 0{,}0630}{\text{weight sample (g)}} \text{ x } 100$$

$$\% \text{ F} = \% \text{ NaF x } 0{,}4524$$

10. References

1. AWWA Standard for Sodium Fluoride, ANSI/AWWA B701-94.
2. “Standard Methods for the Examination of Water and Wastewater”, 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.

8.5.11. SIEVE GRADING FOR SODIUM FLUORIDE

1. Introduction

Sodium fluoride should be supplied as a dry, coarse crystalline material containing no lumps and according to the AWWA Standard for Sodium Fluoride (ANSI/AWWA B701-94) at least 98% should pass through a 850µm sieve, at least 50% should be retained in a 150 µm sieve and not more than 5% should pass through a 45 µm sieve.

2. Scope

This method describes a procedure for the determination of the particle size of sodium fluoride.

3. Interferences

4. Hazards

Sodium fluoride.

Highly corrosive: it is imperative that protective clothing is worn when handling this.

Ensure that you are familiar with the dangers and treatment associated with this substance.

5. Sample Collection and Preservation

Sodium fluoride may be sampled using a sampling tube that is at least 19mm in diameter and should be representative of the entire delivery. Samples must be sealed in airtight and moisture-proof glass or plastic containers. Exposure of the sample to the air must be minimised at all times.

6. Apparatus

1. Analytical balance.
2. Weighing dish or beaker.
3. Sieves of pore size 850 µm, 150 µm and 45 µm.

7. Reagents

None

8. Analytical Procedure

1. Record the mass of the empty weighing dish or beaker and of the sieves.
2. Rapidly weigh out 100,0 g of sample to the nearest 0,1 g.
3. Stack sieves on the bottom receiver pan with the 45 µm sieve at the bottom, then the 150 µm sieve and the 850 µm sieve at the top.
4. Transfer weighed sample onto 850 µm sieve and cover.
5. Screen sample until all three sieves reach constant weight.
6. Weigh sieves (or residue retained on each sieve) or material passing through each sieve to the nearest 0,01 g.
7. Report each portion passing through the sieves or retained on the sieves as a percentage of the total initial sample.
8. The test should be conducted in a dry atmosphere and should be completed as quickly as possible

9. Calculation of Results

$$\% \text{ Retained material} = \frac{(M2 - M1) \times 100}{100}$$

Where:

M1 = mass of empty sieve (g).

M2 = mass of sieve plus residue retained (g).

OR:

$$\% \text{ Material passing through} = \frac{100 - (M2 - M1)}{100} \times 100$$

Where:

M1 = mass of empty sieve (g).

M2 = mass of sieve plus residue retained (g).

10. References

1. AWWA Standard for Sodium Fluorosilicate, ANSI/AWWA B701-94.

8.5.12. INSOLUBLE MATTER IN SODIUM FLUORIDE

1. Introduction

Sodium fluoride should contain at least 97% (dry basis) sodium fluoride or approximately 44% fluoride ions according to the AWWA Standard for Sodium Fluorosilicate (ANSI/AWWA B701-94) and the insoluble matter present in a sample of sodium fluoride should not exceed 0,6%.

2. Scope

This method describes a procedure for the determination of insouble matter present in sodium fluoride.

3. Interferences

4. Hazards

Sodium Fluoride.

Highly corrosive: it is imperative that protective clothing is worn when handling this compound.

Ensure that you are familiar with the dangers and treatment associated with this substance.

5. Sample Collection and Preservation

Sodium fluoride may be sampled using a sampling tube that is at least 19mm in diameter and should be representative of the entire delivery. Samples must be sealed in airtight and moisture-proof glass or plastic containers. Exposure of the sample to the air must be minimised at all times.

6. Apparatus

1. Analytical balance.
2. Oven at 105° C.
3. Desiccator
4. 500 mL beakers
5. Gooch crucibles or fritted-glass filter of medium porosity

7. Reagents

None

8. Procedure

1. Grind approximately 10 g of sample to a powder using a mortar and pestle and then dry at 105° C to constant weight.
2. Weigh 5 g of the ground and dried sample and transfer into a 500 mL beaker.
3. Dissolve in about 400 mL hot distilled water and digest by stirring constantly at a temperature of approximately 90° C for 4 hours, maintaining the original water level by frequent additions of hot distilled water.
4. Filter through a tared Gooch crucible or fritted-glass filter.
5. Wash with at least six separate 25 mL portions of boiling distilled water, allowing the crucible or filter to drain between washings.
6. Dry the crucible or filter at 105° C to constant weight.

9. Calculation

$$\% \text{ Insouble matter} = \frac{M2}{M1} \times 100$$

Where:

M1 = mass of sample (g).

M2 = mass of residue (g).

10. References

1. AWWA Standard for Sodium Fluorosilicate, ANSI/AWWA B701-94

8.5.13. MOISTURE IN SODIUM FLUORIDE

1. Introduction

According to the AWWA Standard for Sodium Fluoride (ANSI/AWWA B701-94) the moisture content should not exceed 0,5% by weight. Caution should be exercised when sampling sodium fluoride to avoid changes in moisture content and samples should be stored in airtight containers, which are only unsealed for sample extraction and then resealed immediately afterwards.

2. Scope

This method describes a procedure for the determination of moisture content in sodium fluoride.

3. Interferences

4. Hazards

Sodium Fluoride.

Highly corrosive: it is imperative that protective clothing is worn when handling this compound.

Ensure that you are familiar with the dangers and treatment associated with this substance.

5. Sample Collection and Preservation

Sodium fluoride may be sampled using a sampling tube that is at least 19 mm in diameter and should be representative of the entire delivery. Samples must be sealed in airtight and moisture-proof glass or plastic containers. Exposure of the sample to the air must be minimised at all times.

6. Apparatus

1. Analytical balance.
2. Desiccator
3. Broad weighing bottle
4. Oven at 105° C

7. Reagents

None

8. Procedure

1. Weigh 5 g of sample to the closest 0,01 g into a weighed broad weighing bottle that has been previously dried and cooled.
2. Heat in the oven at 105° C to constant weight.
3. Cool in a desiccator and reweigh.

9. Calculation

$$\% \text{ Moisture} = \frac{M2 - M3}{M2 - M1} \times 100$$

Where:

M1 = mass of weighing bottle (g).

M2 = mass of weighing bottle and sample before drying (g).

M3 = mass of weighing bottle and sample after drying (g).

10. References

1. AWWA Standard for Sodium Fluorosilicate, ANSI/AWWA B701-94

8.5.14. HEAVY METALS IN SODIUM FLUORIDE

1. Introduction

According to the AWWA Standard for Sodium Fluoride (ANSI/AWWA B701-94), the heavy metals present in sodium fluoride, when expressed as lead, should not exceed 0,04% by weight Atomic absorption spectrometry can be used to determine the heavy metal content of a sodium fluoride sample, but a less accurate, but far simpler titration procedure is described in this manual.

2. Scope

This method describes a procedure for the determination of the heavy metal content of sodium fluoride.

3. Interferences

4. Hazards

1. Sodium Fluoride.

Highly corrosive: it is imperative that protective clothing is worn when handling this compound.

Ensure that you are familiar with the dangers and treatment associated with this substance.

2. Ammonium hydroxide.

Ammonium hydroxide fumes can cause damage to eyes and lungs. Use in well-ventilated area or under a fume hood.

5. Sample Collection and Preservation

Sodium fluoride may be sampled using a sampling tube that is at least 19 mm in diameter and should be representative of the entire delivery. Samples must be sealed in airtight and moisture-proof glass or plastic containers. Exposure of the sample to the air must be minimised at all times.

6. Apparatus

1. Analytical balance.
2. 1 L volumetric flasks
3. 100 mL volumetric flasks
4. 100 mL beakers
5. Platinum dish
6. Fume hood

7. Reagents

1. Ammonium hydroxide, 10%
2. Hydrochloric acid, concentrated
3. Hydrochloric acid 0,1 N
    - Dissolve 8,3 mL of concentrated acid into at least 500 mL distilled water and the dilute to 1 L with distilled water. Always add concentrated acids to water and add slowly, with caution.
4. Hydrogen sulphide, saturated solution
5. Lead nitrate stock solution
    - Dissolve 320,0 mg of reagent grade lead nitrate [$Pb(NO_3)_2$] in 100 mL distilled water containing 1 mL concentrated nitric acid and dilute to 1 000 mL with distilled water.
    - Prepare and store this solution in containers that are free from lead salts.
6. Standard lead solution
    - On the day of analysis, dilute 10,0 mL of the lead nitrate stock solution to 100,0 mL with distilled water (20 mL of this solution contains 0,40 mg of lead, which is equivalent to 0,04% heavy metals in 2,0 g of sodium fluoride).
7. Nitric acid, concentrated

8. Procedure

1. Place 2,0 g of sample that has been previously dried at 105° C to constant weight, in a platinum crucible.
2. Treat this sample with 10 mL concentrated hydrochloric acid.
3. Evaporate contents of platinum crucible to dryness in a fume hood.
4. Repeat the treatment with another 10 mL concentrated hydrochloric acid and again evaporate to dryness in a fume hood.
5. Dissolve the residue in 40 mL of distilled water.

6. Measure out 20 mL of this solution into a 100 mL beaker and adjust to pH 3 to 4 with 10% ammonium hydroxide or 0,1 N hydrochloric acid or both.
7. Add 10 mL of a freshly prepared saturated solution of hydrogen sulphide in distilled water and observe the brown colour formed.
8. Repeat steps 8.6 and 8.7 using 20 mL of the standard lead solution.

9. Result

The brown colour formed using the solution prepared from the sample should not be greater than that formed in the standard lead solution. If it is, then the sample fails the specification.

10. References

1. AWWA Standard for Sodium Fluoride, ANSI/AWWA B701-94
2. Standard Methods for the Examination of Water and Wastewater, 20th Edition, Edited by L. S. Clesceri, A. E. Greenberg and A. D. Eaton, Pub. APHA-AWWA-WEF, 1998.

SODIUM FLUORIDE

Product name	
Plant	
Batch number	
Date delivered to plant	
Date received in laboratory	
Sample number	

STANDARDISATION OF 0,2 N SODIUM HYDROXIDE				
Sample	**Sample Volume**	**Dilution**	**Titre Volume**	**N NaOH**
Blank				
Titre 1				
Titre 2				
Average (- blank)				

FLUORIDE CONTENT			
Sample	**Mass (g)**	**Volume (mL)**	**% NaF**
Blank			
Titre 1			
Titre 2			
Average (- blank)			

SIEVE GRADING				
Sample	**M1 (g)**	**M2 (g)**	**% Retained**	**% Passing**
850 µM				
150 µm				
45 µm				

INSOLUBLE MATTER			
Sample	**M1 Sample (g)**	**M2 Residue (g)**	**% Insoluble Matter**

MOISTURE CONTENT				
Sample	**M1 (g)**	**M2 (g)**	**M3 (g)**	**% Moisture**

HEAVY METALS		
Sample	**Sample: Colour Intensity**	**Std. Lead: Colour Intensity**

9. REFERENCES

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5. American Society for Testing and Materials, Standard Test Method for Particle Size Distribution of Granular Activated Carbon, D 2856-82 (Reapproved 1987).

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