

Cost-Saving and Pollution-Reduction Aspects of the COD Determination

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Abstract

Because of the relatively large amounts of silver and mercury salts used in the COD determination, the disposal of spent solutions from this test presents a significant environmental problem. In addition, the use of silver sulphate as a catalyst in this determination considerably increases the reagent cost. Modifications to the catalyst, the use of smaller sample volumes, and the adoption of procedures for the removal and recovery of silver and mercury from the spent test solutions, are suggested as possible means of reducing both analytical costs and environmental pollution.

Introduction

Chemical oxygen demand (COD), a measure of the oxygen equivalent of that portion of the organic matter in a sample which can be oxidized by a strong chemical oxidant, is a very important parameter for stream and industrial waste studies and in the control of waste treatment plants. (*Standard Methods*, 1975). The method generally approved for the determination of COD in water and wastewater (*Standard Methods*, 1975; ASTM, 1979; EPA, 1979; HMSO, 1977) is the 'dichromate reflux method', in which the sample is oxidized by refluxing with sulphuric acid and standard potassium dichromate solution in the presence of silver sulphate (to catalyse the oxidation of alcohols, and acids of low molecular mass) and mercuric sulphate (to suppress interference due to chloride). The residual dichromate is then determined either by titration with standardized ferrous ammonium sulphate solution, using 1:10 phenanthroline ferrous complex ('ferroin') as indicator, or by spectrophotometry. The amount of oxidizable organic matter in the sample, measured as COD, is proportional to the potassium dichromate consumed.

Unfortunately, this method has the following disadvantages:

- The use of silver sulphate as a catalyst greatly increases the cost of the determination. In January, 1980, the cost of analytical reagent grade silver sulphate was approximately R90 per 100 g. APHA and EPA standard methods, for example, call for the use of 0,75 g of silver sulphate per determination, which means that 68c is added to the cost, giving a total reagent cost per analysis of about R1,05. The ASTM method requires 1 g of silver sulphate, which increases the reagent cost by a further 22c.
- APHA, ASTM and EPA methods also stipulate the use of 1 g of mercuric sulphate per COD determination. Therefore, due to the highly toxic nature of mercury compounds, disposal of spent COD test solutions presents a significant environmental problem. Any form of mercury entering the sewer can be converted by bacterial action into volatile methyl mercury compounds, in which form they are much more toxic than inorganic mercury salts (Dean, Williams and Wise, 1971). For instance, it has been found that 0,03 $\mu\text{g}/\ell$ of methyl mercury in water can be magnified in the food chain in 39 weeks to 500 $\mu\text{g}/\text{kg}$ of mercury in fish tissue (Masselli, Maselli and Burford, 1974).

In a recent interlaboratory comparison study (Smith, 1979), the 36 participating laboratories were requested to give details of their methods of disposal of spent COD test solutions. It was found, that in all but a few cases, these solutions were consigned to the drain. In addition to their extensive use in COD analyses, mercury and silver compounds are used for the analysis of several other determinands in water; e.g. total Kjeldahl nitrogen (digestion step), ammonia (nesslerization method), chloride (argentometric and mercuric thiocyanate methods), and fluoride (preliminary distillation step), as well as for the preservation of water samples for nutrient and demand analyses. Therefore, the total quantity of these compounds discharged to the environment in one year could be as high as several kilograms per laboratory, which leads to the conclusion that laboratories engaged in water and wastewater analysis are themselves significant contributors to mercury and silver enrichment of the environment.

Possible measures for the reduction of analytical costs of the COD determination and for the control of pollution from laboratory wastes containing mercury and silver compounds from COD and other analyses are presented in this paper.

Discussion

Use of an alternative catalyst

The use of silver as a catalyst for the oxidation of organic materials was first reported by Muers (1936), who investigated the catalytic effect of several metals on a variety of pure organic substances, and found that silver was the only metal to produce catalytic activity in the oxidation of acetic acid. Since then, several authors have investigated the necessity of using an effective catalyst in the COD determination, and have invariably re-

commended silver sulphate for this purpose (Moore, Ludzack and Ruchhoft, 1951; Dobbs and Williams, 1963; Burns and Marshall, 1965). Investigations into the effectiveness of other metals as catalysts in this determination (Moore, 1976; Clark and McKinney, 1977) have shown that only manganese and cobalt have any significant value as potential alternatives to silver sulphate. The oxidation ability of these metals, however, is not considered to be sufficiently comparable to that of silver to permit their unequivocal recommendation as catalysts in the determination of COD in water and wastewater.

Moore (1976) investigated the possibility of using less silver sulphate, and found that by reducing the amount of silver sulphate from 22 g/4 kg bottle (the concentration stipulated in most standard texts), to 7.5 g/4 kg bottle, the oxidation efficiency for sodium acetate was lowered by only 3 % (from 98 % to 95 %).

Reduction of analytical costs by the use of a less pure grade of silver sulphate was recommended by Clark and Mitchell (1975), who showed that the use of the considerably cheaper technical grade in place of analytical reagent grade silver sulphate did not significantly affect the results obtained for the COD of various municipal wastewaters.

Use of smaller sample volumes

APHA, ASTM and EPA standard procedures require the use of a 50 ml sample. The APHA method does, however, make provision for smaller sample volumes (down to 10 ml), with corresponding reductions in the quantities of silver and mercuric sulphates. The method recommended in the UK (HMSO, 1977) stipulates a sample volume of 10 ml and the addition of only 150 mg silver sulphate and 200 mg mercuric sulphate. Considerable cost saving and pollution reduction can therefore be effected by the use of techniques requiring smaller sample volumes, and therefore less silver and mercury sulphates.

An even greater reduction in the quantities of silver and mercuric sulphates can be achieved by the application of semi or fully automated techniques. For example, the EPA semi-automated method (EPA, 1979) involves a sample volume of 2.5 ml and only 35 mg of silver sulphate and 50 mg of mercuric sulphate per sample. The National Institute for Water Research (NIWR) fully automated technique (NIWR, 1974), requires only 12 mg of silver sulphate and 0.7 mg of mercuric nitrate per 2.5 ml sample.

The RR method of Ryding and Forsberg (1977) uses *no* mercuric salts and only 27 mg of silver sulphate per 1 ml sample. The sample, plus 2 ml of a potassium dichromate-sulphuric acid-silver sulphate reagent mixture, is autoclaved under pressure for 1 h at 120 °C.

It should be noted, however, that the use of smaller sample volumes may not be advisable in certain cases, e.g. samples containing significant quantities of suspended solids.

Removal and recovery of silver and mercury from spent COD test solutions

In order to reduce pollution risks to the environment, and to recover part of the reagent costs, strong consideration should be given to the removal and possible recovery of silver and mercury from spent COD test solutions.

Silver is best removed by precipitation as the chloride. The following method has been suggested: Place 40 ml hydrochloric acid in a 2 l bottle and add the spent test solutions to the acid. When the bottle is full, allow the silver chloride precipitate

to settle overnight. Decant the supernatant liquid into another container for mercury removal (HMSO, 1977). Filter and wash the silver chloride when a full bottle of precipitate has been collected.

Mercury may be removed by precipitation as the sulphide as follows: Add between 1 and 3 g of stick ferrous sulphide to the decanted liquid from the silver removal stage. Allow to stand for at least 24 h, with occasional swirling or stirring of the solution to disperse hydrogen sulphide, and finally allow the precipitated mercuric sulphide to settle. Decant the supernatant liquid (HMSO, 1977). Hydrogen sulphide is evolved during this process and therefore all operations should be carried out under a fume hood. More detailed procedures for the precipitation of mercury as the sulphide are given by Dean, Williams and Wise (1971), Hautala and McDonald (1978) and EPA (1980). Mercury may also be removed by formation of the chloride complex, followed by collection on an Amberlite IRA-400 ion exchange resin and regeneration (Huibregtse and Moser, 1976).

Certain precious metal refiners in South Africa will accept silver residues for recovery, but at the present time none are known that will accept mercury residues. The latter could be sent to suitable toxic waste disposal sites or converted to mercuric chloride for reuse (EPA, 1980).

Conclusions

With a view to the introduction of cost-saving and pollution-reduction procedures in laboratories involved in water and wastewater analysis, particularly in connection with the COD determination, consideration should be given to the following:

- (a) Reduction in the quantity of silver sulphate used per COD determination and use of cheaper grades of silver sulphate.
- (b) Use of less sample and therefore less silver and mercury sulphates and use of semi-automated or fully automated techniques for COD determination.
- (c) Establishment of suitable procedures for the removal and possible recovery of silver and mercury from spent COD test solutions.

Care should be taken, however, to ensure that any alternative analytical procedures adopted can provide results comparable to those obtained by recognised standard methods, or, if not, results which are acceptable for operational control purposes.

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