J.F. VAN STADEN

DIE OUTO-ANALISERING VAN DIE BEPALING VAN SULFAAT EN ALKALINITEIT IN WATER

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J F van Staden

Departement Chemie
Universiteit van Pretoria
Pretoria, 0002

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OPSOMMING

Betroubare en akkurate inligting omtrent die bestanddele en konsentrasie daarvan in water is van kardinale belang vir besluite rakende watergehalte en aanwending daarvan. Hierdie is 'n saak wat vorentoe meer krities sal word weens die noodsaaklikheid van strenger beheer oor waterbesoedeling. Water bevat egter 'n groot verskeidenheid chemiese verbindings sodat dit bykans onmoontlik is om 'n analitiese metode te gebruik vir die bepaling van hierdie verbindings wat geheel en al vry van steurings is.

Deur analitiese metodes te verbeter, is dit moontlik om die produktiwiteit van 'n laboratorium te verhoog, meer doeltreffende besluite te neem en produksiekostes te besnoei.

'n Opname van die probleme by die grootste laboratoriums wat watergehalte bepaal, het getoon dat prosedures vir die bepaling van alkaliniteit en sulfaat twee van die metodes is wat die meeste probleme skep. In die lig hiervan is ondersoek ingestel na die moontlike verbetering van hierdie metodes.

Op grond van die navorsing word aanbeveel dat :

(1) die enkelpunttitrasiesisteem vir die bepaling van alkaliniteit gebruik word; en

(2) die turbidimetriese metode vir sulfaat met wysigings soos benodig vir die verskillende tipe monsters gebruik word.

(3) Die handloodioonselektiewe elektrode metode vir monsters wat probleme lewer in bogenoemde kolorimetriese metode.

ERKENNING

Die lede van die loodskomitee vir hierdie projek:

Dr W H J Hattingh	-	Waternavorsingskommissie
Prof A Wiechers	-	Universiteit van Pretoria
Dr M J Pieterse	-	Waternavorsingskommissie
Dr F C Viljoen	-	Randwaterraad
Mnr L S Christodoulou	-	Randwaterraad
Dr H R van Vliet	-	Departement van Waterwese
Dr R A van Steenderen	-	Nasionale Instituut vir Waternavorsing
Mnr R Smith	-	Nasionale Instituut vir Waternavorsing
Mnr M L Siebert	-	Nasionale Instituut vir Waternavorsing
Mnr R R Rimmer	-	Johannesburg Munisipaliteit
Mnr M A Behr	-	Johannesburg Munisipaliteit
Mnr R D Morris	-	Suid-Afrikaanse Buro vir Standaarde
Mnr N Penny	-	Departement Gesondheid en Welsyn

het waardevolle leiding en algemene bystand gedurende die verloop van die projek gelewer. Dr W H J Hattingh as voorsitter van die loodskomitee, word hartlik bedank vir die vele ure van vrugbare samesprekings en geduld met die uitvoering van die projek.

Dr H R van Vliet en mnr I Schoonraad van die Hidrologiese Navorsingsinstituut het 'n waardevolle inset gelewer in terme van voorsiening van ge-analiseerde monsters en hulp met oplos van knelpunte in bestaande en voorgestelde prosedures.

Hierdie projek is uitgevoer met finansiële ondersteuning van die Waternavorsings-kommissie, die Wetenskaplike en Nywerheidsnavorsingsraad en die Universiteit van Pretoria.

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INHOUDSOPGAWE

INLEIDING:

Die chemiese samestelling van water speel 'n belangrike rol in die aanwending daarvan. Daarom is betroubare en akkurate inligting omtrent die bestanddele wat in die water is belangrik wanneer besluite geneem moet word of die water geskik sal wees vir die doel waarvoor dit aangewend gaan word. Die ingebruikneming van die rekenaar in die veld van analitiese chemie het meegebring dat 'n aantal analitiese metodes ge-outomatiseer kon word en ook dat inligting vinniger verwerk en gekontroleer kan word. Die analis kan dus tot 'n groot mate vrygestel word van die tydrowende taak van berekening van konsentrasies, die tabelleer van die resultate ens. Hierdie hulpmiddel het dan ook meegebring dat die navorser, wat peil trek op die analitiese resultate, sy werk vinniger kan afhandel met 'n gevolglike toename in die aanvraag na nog meer resultate.

Die outomatisering van analitiese metodes en die versyfering van die resultate met behulp van die rekenaar het dus meegebring dat die doeltreffendheid van die chemiese analis in sommige gevalle vervyfvoudig het.

Dit is gebruiklik om die korrektheid van die anorganiese chemiese analise van water te meet deur 'n katioon/anioonbalans op te stel. Enige analise wat in hierdie toets faal, moet weer herhaal word.

In die meeste analitiese laboratoriums word monsters met 'n groot verskeidenheid chemiese samestellings ontvang en dit is bykans onmoontlik om 'n analitiese metode te gebruik wat geheel en al vry van steurings is. Hierdie eienskap, plus die feit dat monsters met hoë konsentrasies van die bestanddeel dikwels gevolg word deur monsters met baie lae konsentrasies van dieselfde bestand= deel, bring mee dat die katioon/anioonbalans versteur word. In die praktyk beteken dit dat 'n aansienlike aantal monsters weer ontleed moet word. Sodanige heranalise vertraag die monstervloei en die produksievermoë van die laboratorium. Daarbenewens is dit ook uiters neerdrukkend vir die analis om monsters oor en oor te herhaal. Hierdie herhaling beteken ook dat die fondse nie so doeltreffend aangewend word as wat moontlik is nie.

Indien daar besef word dat 'n sulfaatanalise minstens R5 kos en dat van die groter laboratoriums in die land wat water ontleed (Hidrologiese Navorsingsinstituut van die Departement Waterwese, Randwaterraad, Munisipaliteit van Johannesburg en die Nasionale Instituut vir Waternavorsing van die WNNR) ongeveer 100 000 sulke analises per jaar uitvoer, dan is die finansiële implikasies duidelik.

Daar is dus baie meriete daarin om die analitiese metodes te verbeter om sodoende die knelpunte uit te skakel.

Daarom het die Waternavorsingskommissie 'n ooreenkoms met die Universiteit van Pretoria aangegaan waarvolgens die Departement van Analitiese Chemie metodes vir die bepaling van alkaliniteit en sulfaat sou ondersoek, nadat 'n opname by die laboratoriums hierbo genoem, aangetoon het dat hierdie twee metodes die meeste probleme skep.

Die resultate wat tydens hierdie projek verkry is, is onmiddellik verwerk in die vorm van publikasies en van die werk is alreeds gepubliseer of is in die pers. Daarom bestaan hierdie verslag dan net uit bylaes wat die werk en resultate wat verkry is, omskryf. Twee bylaes (nommers 3 en 4) vorm nie deel van die ooreenkoms met die Waternavorsingskommissie nie, maar word ook vir volledigheidshalwe ingesluit.

NAVORSINGSPROGRAM

Alkaliniteit

Die doel van die navorsing was om die akkuraatheid van die metode sodanig te verbeter dat die katioon/anioonbalans betroubaarder is en minder herhalings van analises nodig is.

Die volgende aspekte is gedek:

(1) Verbetering van die bestaande indikator-omslagmetode.

(2) Uitskakeling van organiese materiaal- en kleursteurings.

(3) Ontwikkeling van 'n enkelpunt-titrasiesisteem.

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Sulfaat

Die doel van die navorsing in hierdie geval was om die spoed van die bestaande metode te verhoog, die oordrag van monsters uit te skakel en die drywende onstabiele basislyn te verbeter.

Die volgende aspekte is gedek:

(1) Verbetering van die bestaande metode.

(2) Uitskakeling van organiese materiaal- en kleursteurings.

(3) Ontwikkeling van 'n metode met behulp van ioonselektiewe elektrodes.

RESULTATE

Alkaliniteit

(1) VERBETERING VAN DIE BESTAANDE INDIKATOR-OMSLAGMETODE

Die bestaande indikator-omslagmetode is as volg verbeter:

'n Vinnige (120 monsters per uur) outomatiese metode gebaseer op die beginsels van die vloei-inspuittegniek, gekombineer met die kolorimetriese bromokresol-groenbepaling, is ontwikkel. Tesame met die voordele verbonde aan die vloei-inspuittegniek, is dit 'n verdubbeling in die analisefrekwens van die konvensionele geoutomatiseerde gesegmenteerde kontinue-vloeisisteem. 'n Volledige uiteensetting van die metode is as Bylaag 1 aangeheg.

Die vernaamste voordeel wat uit die voltooiing van fase 1 van hierdie gedeelte spruit, is beter benutting van laboratoriumpersoneel weens die hoër analisefrekwens.

(2) UITSKAKELING VAN ORGANIESE MATERIAAL- EN KLEURSTEURINGS

Kleur en troebelrigheid in sommige monsters kan in bogenoemde metode steur. Hierdie steurings kan verwyder word deur uitskakeling daarvan met behulp van 'n

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outomatiese voorklepsisteem wat bestaan uit geaktiveerde koolstoffiltreer= papier (soortgelyk aan die een wat vir sulfaat gebruik word. Kyk toepaslike Bylaag 5). Die sisteem was egter nie so geslaagd vir alkaliniteit nie. Daar is gevind dat van die komponente betrokke by alkaliniteit in sommige monsters ook verwyder word. Die rede hiervoor is dat van die individuele chemiese spesies van die karbonaatsisteem se ewewig in sommige monsters so krities is dat daar adsorpsie of selfs desorpsie van die komponente wat bepaal word, mag plaasvind.

(3) ONTWIKKELING VAN 'N ENKELPUNT-TITRASIESISTEEM.

Behalwe kleur en troebelrigheid is daar egter 'n aantal matrikse, wat ook in water mag voorkom en wat nog steeds kan steur. Hier word gedink aan afval= materiaal wat chemies kan steur deur die indikator te vernietig. 'n Elek= trometriese enkelpunttitrasiesisteem is ontwikkel na 'n intensiewe studie van die karbonaatsisteem. Die metode is gebaseer op 'n kombinasie van vloei-inspuitanalise en enkelpunttitrasie. Die monster reageer met 'n suurlineêr-gevoelige bufferoplossing en die pH van die resulterende oplossing word met 'n glaselektrode in 'n deurvloeisisteem gemeet. 'n Analisefrekwens van 120 monsters per uur word gehandhaaf. Hierdie metode is baie betroubaarder en akkurater as die indikator-omslagmetode. Steurings soos kleur, troebelrig= heid en chemiese indikatorsteurings word uitgeskakel. 'n Volledige uiteen= setting van hierdie metode is as Bylaag 2 aangeheg.

Sulfaat

(1) VERBETERING VAN DIE BESTAANDE METODE.

Die bestaande metode is soos volg verbeter:

Die analisefrekwens van die bestaande metode is verhoog. Terselfdertyd is die oordrag van monsters uitgeskakel. Die outomatiese bepaling

van sulfaat is hoofsaaklik gebaseer op die meting van die turbiditeit van 'n bariumsulfaatsuspensie. Benewens die korrekte verstrooiing van die lig= deeltjies by 420 nm vir akkuraatheid en presisie, is daar een knellende probleem wat inherent is aan hierdie metode en dit is dat bariumsulfaat= presipitaat in die vloeisel akkumuleer. Dit gee aanleiding tot oordrag van monsters en 'n onstabiele basislyn. Byvoeging van 'n alkaliese buffer-EDTA oplossing deur 'n alternatiewe monsterlus het bogenoemde probleme opgelos. 'n Volledige uiteensetting van hierdie metode is as Bylaag 3 aangeheg.

(2) UITSKAKELING VAN ORGANIESE MATERIAAL- EN KLEURSTEURINGS.

(a) Deur outomatiese voorklepfiltrasie met behulp van 'n tygonbuis gepak met geaktiveerde koolstof.

Daar is egter gevind dat gesuspendeerde vaste deeltjies en die teenwoordigheid van organiese stowwe en kleur steur in bogenoemde bepaling. Hierdie probleem is oorkom deur bogenoemde steurings outomaties te verwyder met behulp van 'n tygonbuis, gepak met geaktiveerde koolstof. Die tygonbuis word in die vloei= sisteem geplaas tussen die monsternemer en die monsternemingsklepsisteem. Die filtreersisteem se nuttige leeftyd word bepaal deur die geaardheid van en aantal vaste deeltjies wat in die monsters teenwoordig is. Daar is gevind dat die sisteem vir meer as 400 bepalings geskik is. Vervanging van die filtreersisteem beïnvloed nie die vloeidinamika van die vermengingsisteem van die vloei-inspuitprosedure nie. 'n Volledige uiteensetting verskyn in Bylaag 4.

(b) Deur outomatiese voorklepfiltrasie met geaktiveerde koolstoffiltreer= papier.

Die vervanging van bogenoemde filtreertygonbuissisteem kan probleme le= wer in roetinelaboratoriums. Die pakking van die buis is tydrowend en die

buis kan te dig gepak word sodat vloeiprobleme ontstaan. Hierdie outomatiese voorklepfiltreersisteem is verder verfyn deur 'n sisteem te ontwikkel waar geaktiveerde koolstoffiltreerpapier gebruik word met die volgende voordele:

* Dit kan maklik vervang word.
* Opeenvolgende sisteme is meer eenvormig.
* Druk en vloei in die verskillende sisteme is meer konstant.

Hierdie sisteem funksioneer goed. Dit kan verder ook vir monsters met ander analiete aangewend word, mits

* gesuspendeerde vaste deeltjies en kleur volledig verwyder kan word sodat dit nie verder steur nie
* akkuraatheid nie beïnvloed word nie
* die monsters nie oplosbare gekleurde deeltjies bevat wat nie verwyder kan word nie. Die sisteem word volledig beskryf in Bylaag 5.

(c) Gebruik van 'n enkel- of dubbelkanaalsisteem by industriële afvalwater.

Sekere watersisteme, veral industriële afvalwater en water vanuit mynhope, bevat komponente wat intens gekleurde oplossings met water vorm. Monsters van 'n soortgelyke aard kom ook voor in watersisteme wat gevoed word vanuit digbeboste gebiede in Suid-Afrika. Daar is gevind dat die kleurstowwe in bogenoemde monsters nie op die geaktiveerde koolstoffiltreerpapier adsorbeer nie. Gevolglik kan die kleur nie op hierdie wyse verwyder word nie. Bogenoemde monsters kom gewoonlik nie as 'n reël op 'n roetine basis in laboratoriums voor nie, maar verskyn soms wel as uitsonderings, gevolglik moet vir sulke monsters voorsiening gemaak word. 'n Analitiese dubbelkanaal- en enkelkanaalsisteem is vir hierdie doel ontwikkel. 'n Volledige uiteensetting word in Bylaag 6 verskaf.

(d) Bepaling van hoë sulfaatinhoud in industriële afvalwater

Enkele monsters veral dié vanaf industriële afvalwater vanuit aanlegte waarin swaelsuur gebruik word, se sulfaatinhoud is relatief hoog sodat dit buite die konsentrasiegebied van bestaande metodes val. Hierdie monsters moet met die hand verdun word voordat die sulfaat bepaal kan word volgens bestaande prosedures. Bogenoemde handverdunningsmetode neem egter baie tyd in beslag en dit kan verder ook lei tot 'n verlaging in akkuraatheid en presisie van resultate.

Outomatiese dialise van monsters het die volgende voordele:

(a) Steuringsmateriaal soos gesuspendeerde deeltjies en organiese kleur word outomaties verwyder.
(b) Verdunning van monsters vind outomaties plaas. Dit skakel sleurwerk uit.
(c) Geen verlies in akkuraatheid en presisie kom voor weens verdunning nie, want elke standaard en monster word onderwerp aan dieselfde konstante vloeidinamika.
(d) Produktiwiteit word verhoog.

Vir meer besonderhede, kyk Bylaag 7.

(3) ONTWIKKELING VAN 'N METODE MET BEHULP VAN IOONSELEKTIEWE ELEKTRODES

Die bepaling van sulfaat is onderworpe aan steurings, wat inherent aan die meettegniek self is. Om al die steurings heeltemal uit te skakel, ver= al kleur en troebelrigheid was dit nodig om na 'n elektrometriese meetsis= teem te beweeg. Daar bestaan wel 'n elektrometriese titrasieprosedure vir die bepaling van sulfaat. Die metode is egter tydrowend.
'n Handmetode vir die indirekte bepaling van sulfaat deur direkte meting met 'n loodioonselektiewe elektrode is ontwikkel. Katione soos Cu^{2+}, Hg^{2+} en Ag^{+}

en anione wat min oplosbare loodsoute vorm (PO_4^{3-}) steur. Die sisteem is bruikbaar vir roetine sulfaatanalises in die gebied 20-200 $mg \cdot dm^{-3}$.

'n Volledige beskrywing van die prosedure en ondersoek is as Bylaag 8 aangeheg.

Outomatisering van bogenoemde handmetode was nie suksesvol nie. Die gevormde $PbSO_4$ bedek die loodioonselektiewe elektrode in die deurvloeisisteem so vinnig dat die sisteem nie reproduseerbaar is nie. Byvoeging van ammoniumasetaat- en ammoniumtartraatoplossings om die sisteem meer reproduseerbaar te maak was nie geslaagd nie.

AANBEVELINGS

Alkaliniteit

Daar word aanbeveel dat die enkelpunt-titrasiesisteem geïmplementeer word vir alkaliniteitsbepalings.

Sulfaat

Die turbidimetriese metode vir sulfaat met wysigings soos benodig vir die verskillende monsters word aanbeveel. Die handloodioonselektiewe elektrode metode word aanbeveel vir monsters wat probleme lewer in bogenoemde kolorimetriese metode met al sy wysigings. Outomatisering van laasgenoemde metode is nie geskik nie.

Die name van sekere kommersiële produkte en instrumentasie wat in die bylaes vermeld is, word nie deur die Waternavorsingskommissie en die Universiteit van Pretoria onderskryf nie.

BYLAAG 1

Vloei-inspuit analise vir die bepaling van die totale alkaliniteit in oppervlakte-, grond- en huishoudelike water volgens die geoutomatiseerde bromokresolgroen metode

J.F. VAN STADEN
Departement Chemie, Universiteit van Pretoria, Pretoria 0002

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H.R. VAN VLIET
Hidrologiese Navorsingsinstituut, Departement Omgewingsake, Privaatsak X313, Pretoria 0001

Abstract

Flow-injection analysis for determining total alkalinity in surface, ground and domestic water using the automated bromocresol-green method

A simple, rapid automated procedure for the colorimetric determination of total alkalinity in surface, ground and domestic water is described. The method is based on the principles of the flow-injection technique in combination with the colorimetric bromocresolgreen indicator determination. The method is suitable for the analysis of total alkalinity at a rate of up to 120 samples per hour with a coefficient of variation of better than 1,40 %. Colour and turbidity in the samples may interfere.

Inleiding

Verskeie metodes is beskikbaar om die korrektheid van mineraalanalises in water te kontroleer (Greenberg en Navone, 1958). In *Standard Methods* (1980) verskyn drie metodes te wete die anioon-katioonbalans, elektriese geleiding en die gebruik van ioonuittuilharse. Alhoewel laasgenoemde twee metodes makliker toegepas kan word, word voorkeur aan die anioon-katioonbalans-metode gegee weens die vollediger mineraalanalises wat terselfdertyd verkry word. Alkaliniteitswaardes vorm sodoende een van die belangrike komponente in so 'n anioon-katioonbalans by natuurlike en afvalwater.

Die pH-waarde van die meeste onbesoedelde omgewingswater lê tussen ongeveer 6,0 en 8,0. Hierdie pH-waarde word primêr deur die chemiese ewewig tussen waterstofkarbonaat- en karbonaatione beheer. Dit word weer gereflekteer in die alkaliniteitwaardes wat verkry word. Die begrip alkaliniteit is in sy totaliteit uiteengesit in *Standard Methods* (1980) en *American Society for testing and Materials* (1975) en word dus nie hier bespreek nie.

Weens die probleme wat ondervind word met die aansluiting van gemeganiseerde titrasieprosedures by vloei-analiseerders, is hoofsaaklik metodes gebruik wat gebaseer is op die verlies of verhoging in absorbansiewaardes in 'n aantal verskillende gebufferde suurbasis/indikatoroplossings wanneer 'n watermonster hierby gevoeg word (Hidrologiese Navorsingsinstituut, 1983). Daar is gevind dat die geoutomatiseerde bromokresolgroen (pH 4,2)-metode die betroubaarste resultate lewer.

Die analisefrekwens van die konvensionele geoutomatiseerde gesegmenteerde kontinue-vloeisisteem is egter net 60 monsters per uur (Hidrologiese Navorsingsinstituut, 1983). Gevolglik is die moontlikheid ondersoek om hierdie frekwens te verhoog en daarom is die vloei-inspuit analisetegniek (VIA) ondersoek. Hierdie tegniek is deur Růžička en Hansen (1975) ontwikkel en is 'n eenvoudige en gerieflike konsep van kontinue vloei-analise. Die tegniek is in staat om analisefrekwensie in die meeste roetine laboratoriums te verhoog.

Die voordele van hierdie tegniek is volledig bespreek in oorsigartikels deur Růžička en Hansen (1980, 1981), Betteridge (1978), Ranger (1981) en Van Staden (1981, 1983).

Hierdie artikel beskryf 'n vloei-inspuitprosedure vir die bepaling van totale alkaliniteit in oppervlakte-, grond- en huishoudelike water volgens die geoutomatiseerde bromokresolgroenmetode.

Beginsel van die geoutomatiseerde metode

Bromokresolgroen word as die suur-basis indikator in die metode gebruik aangesien die pH-gebied (3,6 – 5,2) daarvan met die ekwivalentepunt van totale alkaliniteit ooreenstem. Dit lewer verder 'n definitiewe kleurverandering (geel na blou) wat gerieflik kolorimetries gemeet kan word. Die bromokresolgroen word in 'n buffer (pH 4,0) opgelos waarvan die bufferkapasiteit sodanig gekies is dat die byvoeging van alkaliniteit die pH-waarde min verander en dus 'n verandering in kleur van die suurbasis indikator tot gevolg het. Monsters moet nie verdun, gekonsentreer of op enige manier verander word nie.

Eksperimenteel

Apparaat

(i) *Monsternemingsklep*

'n Carle mikrovolume tweeposisie monsternemingsklep (Carle Katalogusnommer 2014) met twee monsternemingslusse is gebruik. Die klepsisteem is gesinchroniseer met die monsternemingseenheid. 'n Peristaltiese pomp voorsien die draerstroom teen 'n konstante vloeitempo.

(ii) *Cenco monsternemer.*

basiese inligting met behulp waarvan die lang termyn gemiddelde jaarlikse vloedskade bepaal kan word. Hierdie lang termyn gemiddelde jaarlikse vloedskade word dan in vloedskadebeheerbeplanningsmodelle as uitgangspunt geneem vir die vasstelling van die voordele wat met verskillende kombinasies van vloedskadebeheermaatreëls verkry sal word (Viljoen, 1979).

Samevatting en gevolgtrekking

Vanweë die potensiaal van vloedskadevoorspellingsmodelle om toekomstige vloedskade te beraam en as nodige inset om vloedskadebeheermaatreëls te beplan, is gepoog om aan die hand van inligting wat na werklike vloede bekom is, sodanige modelle te ontwikkel. By die ontwikkeling van die modelle is klem op formele modelle gelê, veral vanweë die potensiaal wat die modelle het om vloedskade ook in ander trajekte te beraam. Die vernaamste bevindings ten opsigte van die formele modelle is as volg (Smith, *et al.*, 1981):

- Dit was nie moontlik om data ten opsigte van alle ter sake vloedkenmerke, byvoorbeeld sleurkrag en slikinhoud van die vloedwaters, te bekom nie. Die enigste twee vloedveranderlikes waarvoor redelike akkurate data bekom kon word, is oppervlakte en diepte oorstroom. Beskikbare data ten opsigte van sekere veranderlikes, soos duurte van oorstroming, was nie altyd voldoende akkuraat nie.
- Voldoende data vir die ontwikkeling van formele verliesfunksies was slegs vir 'n paar riviertrajekte en skadekategorieë beskikbaar. Die skadekategorieë is enkelverdiepingwoonhuise, 'n paar ander tipes geboue, akkergewasse, wingerde en besproeiingsgrond.
- Omdat alle ter sake fisiese vloedkenmerke nie in die modelle opgeneem kon word nie, was dit in die meeste gevalle nie moontlik om algemeen toepaslike verliesfunksies te bepaal nie. Die enigste skadekategorieë waarvoor modelle bepaal kon word wat ook op ander trajekte toepassingswaarde het, is enkelverdiepingwoonhuise en buitegboue.
- Die twee fisiese vloedveranderlikes wat die sterkste in die formele modelle figureer is oppervlakte en diepte oorstroom. By gewasskade is dit oppervlakte oorstroom terwyl dit by grond- en gebouskade beide is.

Gegewe die probleme om 'n volledige stel formele verliesfunksies te bepaal, is 'n stel informele funksies gekonstrueer. Met die funksies, wat bloot die klassifisering van alle direkte vloedskade in diepte-oorstroomintervalle behels, kan die skade van vloede van verskillende omvang vir 'n betrokke trajek, met die nodige aanpassings en veronderstellings, beraam word. Die modelle se gebruikswaarde is noodwendig beperk tot die trajekte waarvoor dit bepaal is. Ook sal die aanwendbaarheid van die modelle om toekomstige vloedskade te voorspel vinnig afneem wanneer die grondgebruiksamestelling in die vloedvlakte verander.

Hoewel informele modelle dus nie as 'n volledige alternatief vir formele modelle beskou kan word nie, het die ontwikkeling van die modelle besliste meriete in die navorsing na vloedskadevoorspellingsmodelle, veral vir vloedgebiede waarvoor optimale vloedskadebeheermaatreëls beplan moet word.

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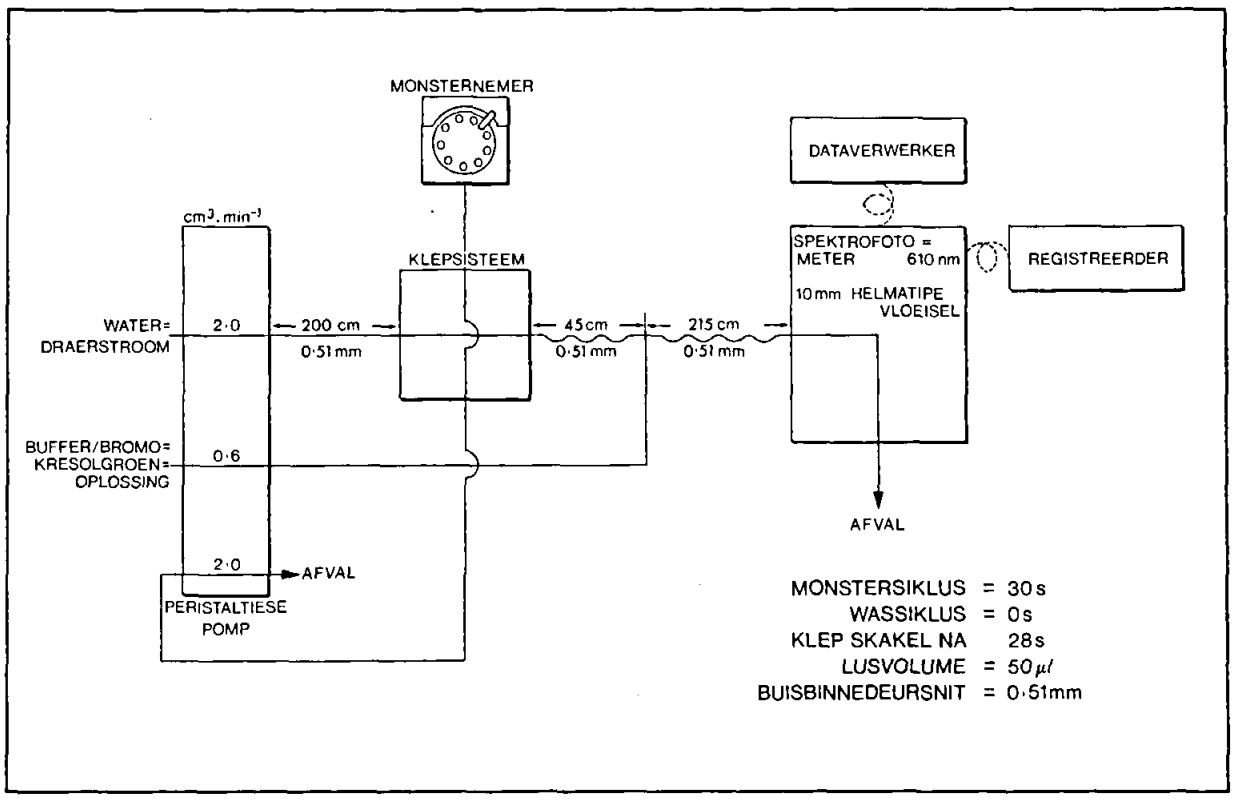


Figuur 1
Vloeidiagram vir totale alkaliniteit. Analisefrekwens 120 monsters per uur. Buislengte en -binnedeursnit word respektiewelik in cm en mm gegee.

(iii) ***Cenco peristaltiese pomp wat teen 10 revolusies per minuut funksioneer.***

(iv) *Vermengingsisteem* (Fig. 1).

(v) *Spektrofotometer*

Bausch en Lomb Spectronic 21 DV spektrofotometer (Rochester, New York) toegerus met 'n 10 mm Helma tipe deurvloeisel (volume 80 µℓ).

(vi) ***Mettler Model GA 12 registreerder.***

Reagense

Analities reagens-graad reagense is gebruik, tensy dit anders gespesifiseer is.

(i) *Natriumhidroksiedoplossing*

Los 6,6 g natriumhidroksied in gedistilleerde water op en verdun kwantitatief na 500 cm³. Berg die oplossing in 'n poli-etileenhouer.

(ii) *Bromokresolgroen-stamoplossing*

Voeg 14,5 cm³ van bogenoemde natriumhidroksiedoplossing by 800 cm³ gedistilleerde water. Meng goed. Los 3 g bromokresolgroen hierin op en verdun na 1 dm³. Berg die oplossing in 'n donker glashouer by 4°C. Die oplossing is stabiel vir 5 dae.

(iii) *Buffer/bromokresolgroenoplossing*

Los agtereenvolgens 1 g kalsiumchlorieddihidraat ($CaCl_2 \cdot 2H_2O$) en 15 g kaliumwaterstofftalaat ($C_8H_5O_4K$) op in 800 cm³ gedistilleerde water. Voeg 40 cm³ bromokresolgroen-stamoplossing by. Stel die pH in op 4 met 'n 1 mol·dm^{-3} HCl-oplossing (of 'n 1 mol·dm^{-3} NaOH-oplossing) en verdun na 1 dm³. Hierdie oplossing is stabiel vir 2 dae.

Standaarde

(i) *Stam-waterstofkarbonaatoplossing*

Los 6,7480 g natriumwaterstofkarbonaat ($NaHCO_3$), gedroog vir 1 uur by 60°C, in gedistilleerde water op. Verdun kwantitatief na 1 dm³. Hierdie oplossing is ekwivalent aan 'n oplossing wat 4 mg kalsiumkarbonaat ($CaCO_3$) in 1 cm³ bevat.

(ii) *Standaard-waterstofkarbonaatoplossings*

Berei die volgende reeks standaardoplossings in 1 dm³ volumetriese flesse.

Nommer	Volume stamoplossing (cm³)	$CaCO_3$-konsentrasie in mg·dm^{-3}
1	10,0	40
2	30,0	120
3	50,0	200
4	80,0	320
5	100,0	400

Monsterpreservering

Preserveer die monsters met 20 mg Hg(II) per dm^3 monster. Die monsterbottels moet heeltemal gevul wees en moet so min moontlik voor analise oopgemaak word.

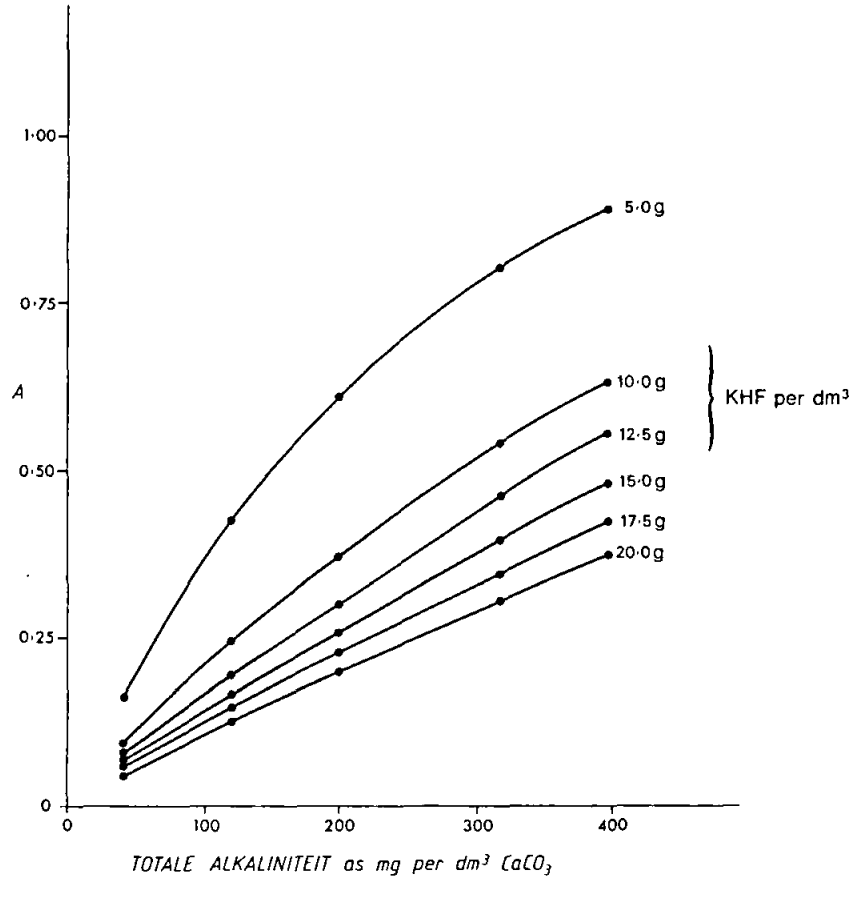
Analitiese vloeisisteem

'n Skematiese diagram van die analitiese vloeisisteem word in Fig. 1 aangetoon. Die vermengingsisteem bestaan uit Tygonbuise met 'n binnedeursnee van 0,51 mm. Die buise is as vermengingspoele om 15 mm perspexstawe gedraai. Lynlengtes word in Fig. 1 aangedui. 'n Cenco peristaltiese pomp, wat teen 10 revolusies per minuut funksioneer, voorsien die draer- en reagensstrome teen konstante vloeitempo's. Monsters van 'n outomatiese Cenco monsternemer word outomaties met behulp van 'n 50 μl monsterlus in die draerstroom ingelaat. 'n Monstersiklus van 30 s word tussen opeenvolgende monsters gehandhaaf. Dit gee 'n analisefrekwens van 120 monsters per uur. Die monsternemingsklepsisteem skakel elke 28 s nadat die monsternemer na die volgende monster beweeg het. Die klepsisteem is gesinchroniseer met die monsternemingseenheid.

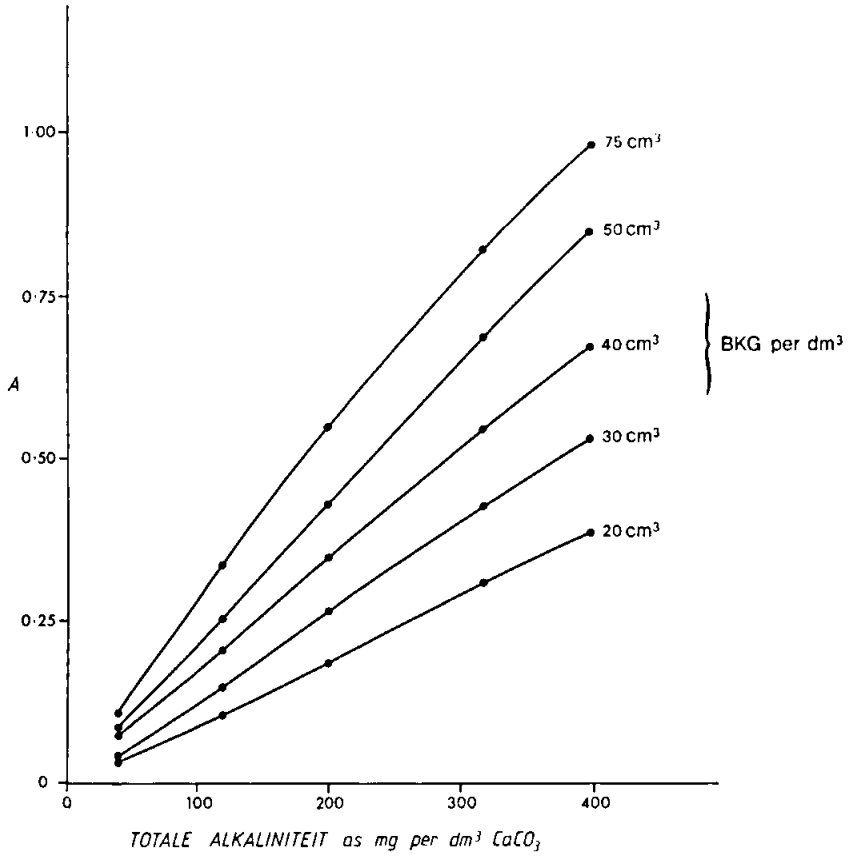
Resultate en bespreking

Die bufferkapasiteit van die vloeistroom in die deurvloeidetektor beïnvloed die lineariteit van die bepaling. Die bufferkapasiteit is 'n funksie van die bufferkonsentrasie. Die bufferkonsentrasie in die omgewing van die deurvloeisisteem word deur die draerstroomvloeitempo, bufferstroomvloeitempo en die reagensbottel se bufferkonsentrasie beheer. Daar is besluit om eers die konsentrasies van die verskillende komponente in die buffer/bromokresolgroenoplossing te optimiseer. Resultate toon dat die kalsiumchlorieddihidraatkonsentrasie die absorbansie min beïnvloed. 'n Konsentrasie van 1 g $CaCl_2 \cdot 2\ H_2O$ per dm^3 oplossing lewer die beste reproduseerbare resultate. Die invloed van kaliumwaterstofftalaatkonsentrasie verskyn in Fig. 2. 'n Monstergrootte van 50 μl, draerstroomvloeitempo van 2,00 $cm^3 \cdot min^{-1}$ en bufferstroomvloeitempo van 0,60 $cm^3 \cdot min^{-1}$ is gebruik by bogenoemde optimiseringstudie. Die resultate toon duidelik dat die bufferkapasiteit van kaliumwaterstofftalaatkonsentrasies laer as 15 g per dm^3 nie voldoende is om hoë alkaliniteitwaardes te hanteer nie. Gevolglik krom die lyn by hoë waardes. Daar is gevind dat 'n kaliumwaterstofftalaatkonsentrasie van 15 g per dm^3 die beste resultate lewer ten opsigte van presisie en lineariteit.

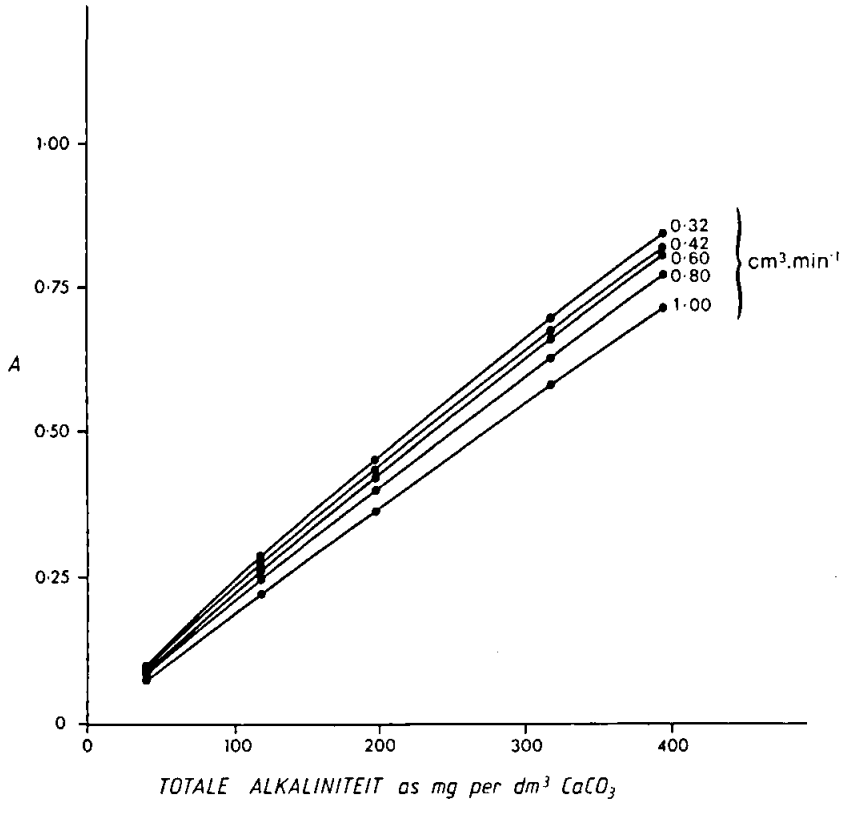
Optimisering van die bromokresolgroenkonsentrasie (Fig. 3) met 'n monstergrootte van 50 μl, draerstroomvloeitempo van 2,00 $cm^3 \cdot min^{-1}$ en bufferstroomvloeitempo van 0,60 $cm^3 \cdot min^{-1}$ toon dat 40 cm^3 van die bromokresolgroenstamoplossing per dm^3 die beste resultate lewer. By 50 cm^3 verswak die presisie terwyl 'n kromme by hoër konsentrasies voorkom. Bogenoemde geoptimiseerde konsentrasies van die komponente in die buffer/bromokresolgroenoplossing is by die verdere evaluering-



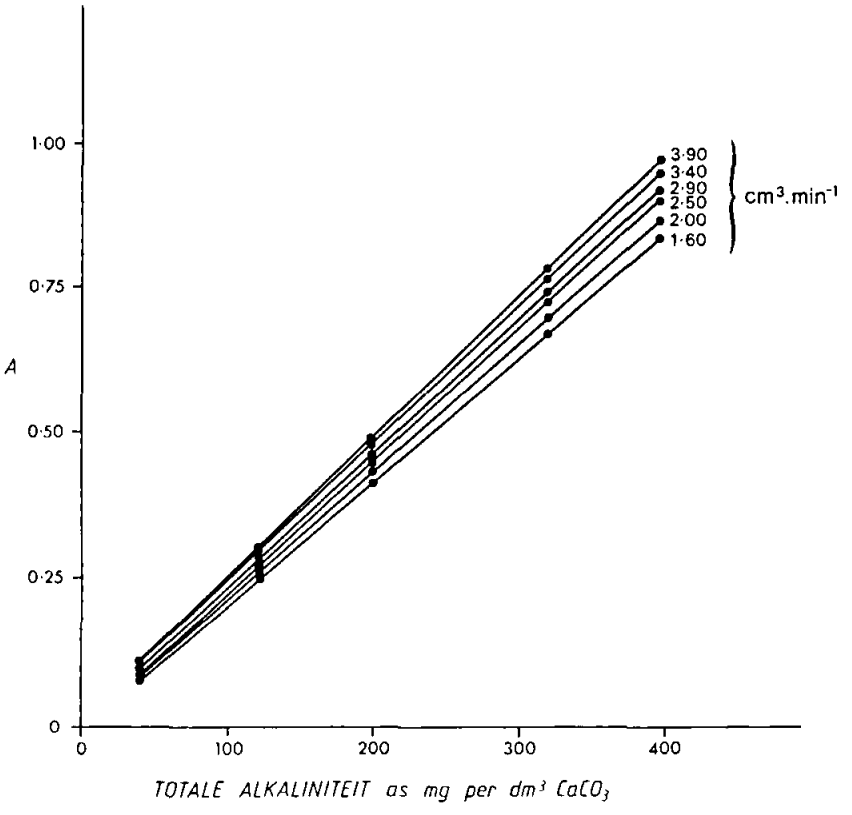
Figuur 2
Invloed van kaliumwaterstofftalaatkonsentrasie (KHF). Monstergrootte = 50 μl. Draerstroomvloeitempo = 2,00 $cm^3 \cdot min^{-1}$. Bufferstroomvloeitempo = 0,60 $cm^3 \cdot min^{-1}$.



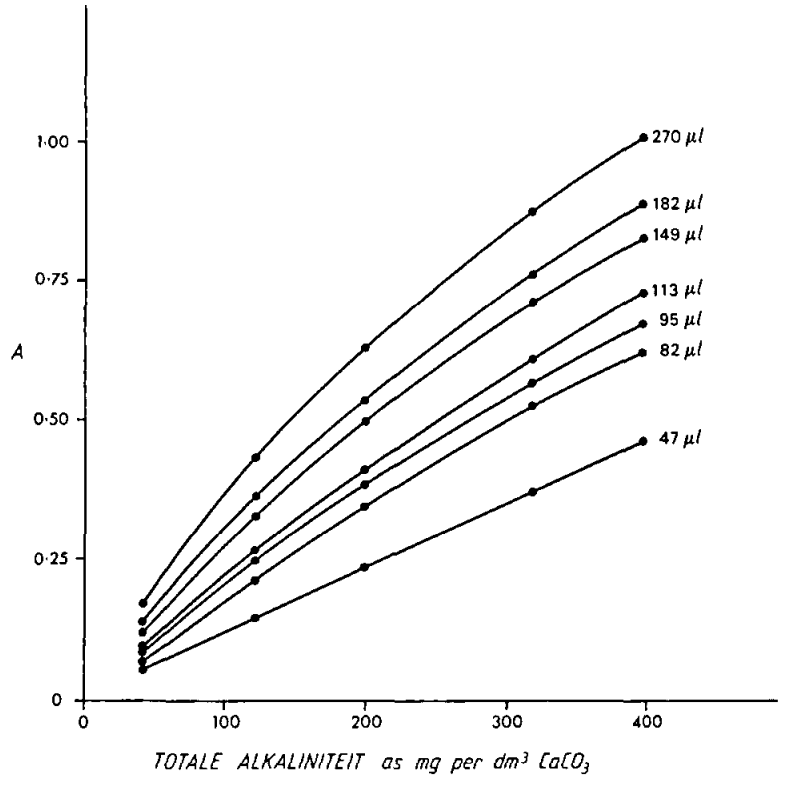
Figuur 3
Invloed van bromokresolgroenkonsentrasie (BKG). Monstergrootte = 50 µℓ. Draerstroomvloeitempo = 2,00 $cm^3 \cdot min^{-1}$. Bufferstroomvloeitempo = 0,60 $cm^3 \cdot min^{-1}$.



Figuur 4
Invloed van bufferstroomvloeitempo. Monstergrootte = 80 µℓ. Draerstroomvloeitempo = 2,00 $cm^3 \cdot min^{-1}$.



Figuur 5
Invloed van draerstroomvloeitempo. Monstergrootte = 80 µℓ. Bufferstroomvloeitempo = 0,60 $cm^3 \cdot min^{-1}$.



Figuur 6
Invloed van monstervolume. Draerstroomvloeitempo = 2,00 $cm^3 \cdot min^{-1}$. Bufferstroomvloeitempo = 0,60 $cm^3 \cdot min^{-1}$.

TABEL 1
RESULTATE VAN DIE PRESISIETOETS VIR DIE VOORGESTELDE VIA METODE SOOS UITGEVOER OP 'N REEKS TOTALE ALKALINITEIT STANDAARDOPLOSSINGS

Monster	Totale alkaliniteit as $mg \cdot dm^{-3}$ $CaCO_3$	Variasiekoëffisiënt[a] %
1	40	1,40
2	120	0,80
3	200	0,58
4	320	0,39
5	400	0,36

[a]Vir 14 toetse in elke geval

TABEL 2
VERGELYKING VAN RESULTATE VERKRY MET 'N STANDAARD OUTOMATIESE GESEGMENTEERDE METODE EN DIE VOORGESTELDE VLOEI-INSPUIT METODE (VIA)[a]

Monster	Gesegmenteerde metode	VIA	Variasiekoëffisiënt %
1	161	156	0,64
2	150	146	0,71
3	43	42	1,34
4	161	160	0,69
5	48	47	1,23
6	27	32	1,37
7	95	95	0,87
8	34	32	1,39
9	40	34	1,29
10	27	34	1,31
11	100	90	0,90
12	341	337	0,38
13	82	76	0,93
14	99	95	0,89
15	66	63	0,99
16	64	64	0,96
17	54	52	1,09
18	257	254	0,49
19	20	24	1,39
20	25	24	1,37
21	254	241	0,47
22	119	115	0,84
23	61	52	1,07
24	47	44	1,19
25	250	254	0,51

[a]Gemiddelde resultaat van 14 toetse in elke geval

TABEL 3
VERGELYKING VAN RESULTATE VERKRY MET DIE VOORGESTELDE VIA METODE SONDER EN MET DIE STANDAARD ADDISIEMETODE

Monster	VIA sonder standaard addisie	VIA met standaard addisie	Herwinbaarheid (%)
1	254	250	98,4
2	160	157	98,1
3	64	63	98,4
4	115	115	100,0
5	34	36	105,8
6	95	93	97,9

weglaatbaar klein. Geen basislyndryf is ondervind nie. Daar is wel gevind dat kleur en troebelrigheid in die monsters in hierdie metode kan steur. Van die reeks van 67 monsters wat ontleed is het net een die probleem gelewer. Resultate het verder getoon dat die waardes van sommige monsters wel betekenisvol kan wissel indien die monsterbottels te veel oopgelaat en aan die atmosfeer blootgestel word.

Die presisie van die metode is op standaarde (Tabel 1) en op watermonsters getoets (Tabel 2). Die standaardafwyking is minder as 1,40% vir 14 toetse op elke watermonster.

Die voorgestelde VIA metode vergelyk verder gunstig met die standaard outomatiese gesegmenteerde metode (Hidrologiese Navorsingsinstituut 1983 (Tabel 2). Die akkuraatheid van die voorgestelde metode is ook getoets deur die standaard addisiemetode. Bekende hoeveelhede totale alkaliniteit is by watermonsters gevoeg en die resultate voor en na addisie is verwerk. Die waardes wat verkry is deur die voorgestelde metode en dié deur die standaard addisie modifikasie, verkyn in Tabel 3. Dit blyk duidelik dat die herwinbaarheid voldoende is. Die herwinbaarheid van die voorgestelde metode oor vyf dae is ook getoets. Kontrole monsters is oor 'n tydperk van vyf dae teen standaardoplossings geëvalueer. Herwinbaarheid was beter as 99 %.

Die VIA metode wat hier beskryf word, is geskik vir die bepaling van totale alkaliniteit teen 'n tempo van 120 monsters per uur met 'n variasiekoëffisiënt van beter as 1,40 %.

Erkenning

Hierdie projek is uitgevoer met finansiële ondersteuning van die Waternavorsingskommissie, die Wetenskaplike en Nywerheidnavorsingsraad en die Universiteit van Pretoria.

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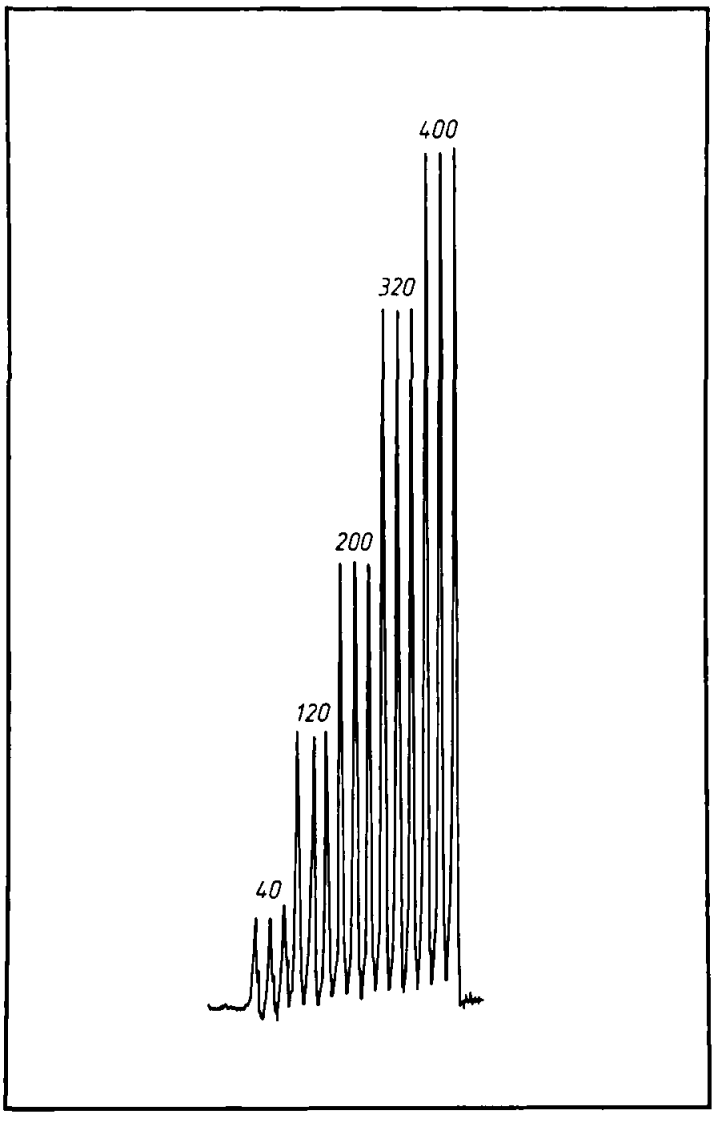
studies gebruik. Die evaluering van die bufferstroomvloeitempo word in Figuur 4 aangetoon. 'n Monstergrootte van 80 $\mu\ell$ en 'n draerstroomvloeitempo van 2,00 $cm^3 \cdot min^{-1}$ is by die evaluering gebruik. Lineariteit word verkry vir bufferstroomvloeitempo's groter as 0,60 $cm^3 \cdot min^{-1}$. By vloeitempo's kleiner as 0,60 $cm^3 \cdot min^{-1}$ wyk die lineariteit af vir lae alkaliniteitswaardes. By bufferstroomvloeitempo's groter as 0,80 $cm^3 \cdot min^{-1}$ verswak die presisie betekenisvol weens die hoër vloeitempo in die betrokke lynlengte en gevolglike swakker mengbaarheid. 'n Bufferstroomvloeitempo van 0,60 $cm^3 \cdot min^{-1}$ lewer die beste resultate. Die draerstroomvloeitempo beïnvloed nie net die presisie en lineariteit van die metode nie, maar beheer ook die analisefrekwens van die watermonsters. Die absorbansie word nie veel deur verandering in vloeitempo beïnvloed nie; die presisie wel. Alhoewel 'n draerstroomvloeitempo van 2,5 $cm^3 \cdot min^{-1}$ (Fig. 5) 'n hoër analisefrekwens lewer en nog steeds lineêr is, is gevind dat 'n hoër presisie met 'n draerstroomvloeitempo van 2,0 $cm^3 \cdot min^{-1}$ verkry word.

Monstervolume beïnvloed ook lineariteit en presisie. In die geval van 'n propinspuiting word 'n skyf met lengte ΔL van die draerstroom oombliklik verplaas deur monstervloeistof met beginkonsentrasie, C_o. L is die lynlengte van die hele sisteem. Die hoeveelheid monster Q_o wat in die draerstroom ingelaat word is

$$Q_o = \pi R^2 \Delta L\, C_o$$

waar R die straal van die monsterbuis is. Die lengte van die monsterskyf ΔL en die straal van die monsterskyf R beïnvloed dus die presisie van die metode. Die beste resultate is verkry met 'n monstergrootte van 50 μl (Fig. 6). Die resultate van die triplikaatanalise van 'n reeks totale alkaliniteit standaardoplossings verskyn as 'n tipiese verteenwoordigende strookkaart registreerder uitdruk in Fig. 7. Analisetempo is 120 monsters per uur.

Die invloed van monsteroordrag is geëvalueer deur analises na willekeur uit te voer. Oordrag van een monster na 'n tweede is



Figuur 7
Resultate van die triplikaatanalise van 'n reeks totale alkaliniteit standaardoplossings. Die getalle op die pieke dui die totale alkaliniteit as mg per dm^3 $CaCO_3$ aan.

BYLAAG 2

VLOEI-INSPUIT ANALISE VIR DIE TOTALE ALKALINITEIT IN OPPERVLAKTE-, GROND- EN HUISHOUDELIKE WATER MET BEHULP VAN 'N ENKELPUNTTITRASIESISTEEM

J.F. VAN STADEN

Departement Chemie

Universiteit van Pretoria

PRETORIA 0002

ABSTRACT

An electrometric single-point titration system for the determination of total alkalinity in surface-, ground- and domestic water is described. The method is based on a combination of flow-injection analysis and single-point titration. The sample is reacted with an acid linear-response buffer solution and the pH of the resulting solution is measured with a glass electrode in a flowthrough assembly. The method is suitable for the analysis of total alkalinity at a rate of up to 120 samples per hour with a coefficient of variation of better than 0,8%. Interferences like colour and turbidity are eliminated.

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SAMEVATTING

'n Elektrometriese enkelpunttitrasiesisteem vir die bepaling van totale alkaliniteit in oppervlakte-, grond- en huishoudelike water word beskryf. Die metode is gebaseer op 'n kombinasie van vloei-inspuit analise en enkelpunt= titrasie. Die monster reageer met 'n suur lineêr gevoelige bufferoplossing en die pH van die resulterende oplossing word met 'n glaselektrode in 'n deurvloeisisteem gemeet. Die metode is geskik vir die analise van totale alkaliniteit teen 'n tempo van tot 120 monsters per uur met 'n variasie= koëffisiënt van beter as 0,8%. Steurings soos kleur en troebelheid word uitgeskakel.

INLEIDING

Die karbonaatsisteem vorm die belangrikste suur-basissisteem in natuurlike water. Die chemiese spesies waaruit die karbonaatsisteem bestaan naamlik koolstofdioksied in die gasvorm ($CO_2(g)$), waterige of opgeloste koolstof= dioksied ($CO_2(aq)$), karboonsuur ($H_2CO_3(aq)$), waterstofkarbonaat ($HCO_3^-(aq)$), karbonaat ($CO_3^{2-}(aq)$) en karbonaatbevattende vaste stowwe omvat een van die hoofsuur-gekonjugeerde basissisteme in natuurlike water. Die karbonaatspesies buffer verder ook natuurlike water. Weens die invloed van die karbonaat= sisteem op die suur-basis eienskappe van water is die analitiese tegnieke wat die kapasiteit van water in terme van alkaliniteit bepaal, grootliks gebaseer op die spesifieke eienskappe van die karbonaatsisteem. As gevolg hiervan vorm alkaliniteitswaardes 'n belangrike kontrolepunt in die beheer en interpretasie van die katioon/anioonbalans by natuurlike en afvalwater.
In bogenoemde watersisteme neem die individuele chemiese spesies van die karbonaatsisteem verder ook deel aan ander belangrike reaksies wat streng gesproke nie suur-basis interaksies is nie. Dit verander egter wel die alkaliniteitswaardes. Voorbeelde van reaksies wat hierdie katioon/anioon= balans versteur, is onder andere

(a) Deelname van koolstofdioksied in die biologiese respirasieproses en oksidasie van organiese materiaal (CO_2 word gevorm).

(b) Deelname van koolstofdioksied in biosintese deur fotosintetiese organismes (CO_2 word verbruik).

(c) Reaksies tussen karbonate en waterstofkarbonate aan die een kant met metale soos onder andere Ca^{2+} en Mg^{2+}.

4 / ...

(d) Chemiese behandeling van harde water en industriële afvalwater.

(e) Heterogene gas-vloeistofewewigreaksie van koolstofdioksied (oplos van CO_2 en omgekeerde).

Bogenoemde reaksiesisteme lei daartoe dat die alkaliniteit van water die geskiktheid daarvan vir besproeiing, industriële en huishoudelike gebruik beïnvloed.

Die alkaliniteit van water word gedefinieer as die kapasiteit van sommige bestanddele om 'n sterk suur te neutraliseer. In natuurlike water is hierdie kapasiteit hoofsaaklik te wyte aan basisse soos HCO_3^- , CO_3^{2-} en OH^- en in 'n mindere mate spesies met kleiner konsentrasies soos silikate, borate, ammoniak, fosfate en organiese basisse. Die ekwivalente hoeveelheid sterk suur wat benodig word om hierdie ione te neutraliseer is gelyk aan die totale alkaliniteit. By oppervlaktewater word die alkaliniteitwaarde hoof= saaklik aan die konsentrasie van die karbonaat-, waterstofkarbonaat- en hidroksiedinhoud toegeskryf.

In die praktyk sluit 'n alkaliniteitbepaling die titrasie met 'n standaard suur soos soutsuur of swaelsuur in (Standard Methods for the Examination of Water and Wastewater, 1980) en dit reflekteer die algehele konsentrasie van bestanddele wat in staat is om met waterstofione onder die titrasietoestande te reageer. Eksperimenteel word die hidroksied-, waterstofkarbonaat- en karbonaatalkaliniteit bepaal deur agtereenvolgens die oplossing eers te titreer na die waterstofkarbonaat-endpunt en dan na die karboonsuur- of totale alkaliniteit-endpunt. Fenolftaleïenindikator word vir waterstofkar= bonaat-endpunt en metieloranje indikator vir die totale alkaliniteit-endpunt gebruik. Die H^+-ione van die sterk suur, wat bygevoeg word, is die stoïgio=

metriese hoeveelhede vir die volgende reaksies:

$$H^+(aq) + OH^-(aq) \rightleftarrows H_2O(\ell)$$
$$H^+(aq) + HCO_3^-(aq) \rightleftarrows H_2CO^*{}_3(aq)$$
$$2\ H^+(aq) + CO_3^{2-}(aq) \rightleftarrows H_2CO_3^*(aq)$$

($H_2CO_3^*$ is onstabiel en ontbind om CO_2 en H_2O te vorm)

Hiervolgens word totale alkaliniteitwaarde gegee deur:

Totale alkaliniteit

$$= [HCO_3^-] + 2\ [CO_3^{2-}] + [OH^-]$$

'n Alkaliniteit titrasiekromme word in Figuur 1 aangetoon. Daar bestaan 'n hele aantal moontlike kombinasies van die waterstofkarbonaat-, karbonaat- en hidroksiedioonkonsentrasies wat aanleiding gee tot kenmerkende titrasie= krommes. Met Figuur 1 as verwysing kan die alkaliniteitwaarde soos volg toegeskryf word.

1. Indien a > b.

   (i) Wanneer b = 0. In hierdie geval sal die totale alkaliniteit vir alle praktiese doeleindes gelyk wees aan die hidroksiedkonsentrasie.

   (ii) Wanneer b > 0. In hierdie geval sal die totale alkaliniteit gelyk wees aan die teenwoordigheid van hidroksied- en karbonaatalkaliniteit.

2. Indien a = b. Die totale alkaliniteit word deur die karbonaatione verteenwoordig.

3. Indien a < b.

   (i) Wanneer a > 0. Dit dui op die teenwoordigheid van die waterstof= karbonaat- en karbonaatalkaliniteit.

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(ii) Wanneer a = 0. In hierdie geval sal die totale alkaliniteit vir alle praktiese doeleindes gelyk wees aan die waterstofkarbonaatioonkonsentrasie.

Bogenoemde verwantskappe geld solank as wat daar geen ander swak sure of basisse in die water teenwoordig is nie. Die ewewig

$$CO_2(g) \rightleftarrows CO_2(aq) \rightleftarrows H_2CO_3(aq)$$

behoort ook indirek die totale alkaliniteitwaarde te beïnvloed. Totale alkaliniteit is egter 'n behoudende eienskap van water en word derhalwe nie beïnvloed deur relatief klein skommelings in temperatuur en druk nie of deur die byvoeging of verwydering van relatief klein hoeveelhede koolstofdioksied nie. Indien 'n klein hoeveelheid koolstofdioksied by 'n oplossing gevoeg word, sal die pH van die oplossing verlaag en die waterstofkarbonaatkonsentrasie toeneem met 'n stoïgiometriese hoeveelheid.

$$CO_2(g) + H_2O(\ell) \rightleftarrows HCO_3^-(aq) + H^+(aq)$$

Indien 'n klein hoeveelheid koolstofdioksied uit die water verlore gaan, sal die pH toeneem en 'n stoïgiometriese hoeveelheid karbonaatione sal omgeskakel word na waterstofkarbonaat- en hidroksiedione.

$$H_2CO_3(aq) \rightleftarrows H_2O(\ell) + CO_2\uparrow$$

$$CO_3^{2-}(aq) + H_2O(\ell) \rightleftarrows HCO_3^-(aq) + OH^-(aq)$$

Indien 'n watersisteem dus in ewewig met sy omgewing is, sal die byvoeging of verwydering van relatief klein hoeveelhede koolstofdioksied wel die pH en die spesiering van die ione in die water beïnvloed, maar geen noemenswaardige invloed op die totale alkaliniteit uitoefen nie. Dit het daartoe gelei dat dit wel moontlik is om totale alkaliniteit in water te bepaal.

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Die drastiese versteuring van die ewewigsisteem en die byvoeging of ont= trekking van relatief groot hoeveelhede koolstofdioksied beïnvloed wel die totale alkaliniteitwaarde soos in die geval van boorgatwater. Die geleidelike onttrekking of byvoeging van koolstofdioksied lewer dieselfde resultate. Gevolglik kan monsterhouers nie relatief lank oopgelaat word nie.

Die standaard prosedures (Standard Methods for the Examination of Water and Wastewater, 1980;- American Society for Testing and Materials, 1975) vir die bepaling van totale alkaliniteit in water kan in die volgende twee kategorieë geplaas word naamlik elektrometriese (potensiometriese) titrasies en kleurver= andering (kleurvergelykende) titrasies. Van hierdie twee kategorieë word die mees presise en akkurate resultate gegee deur elektrometriese titrasies. Kleurverandering of kleurvergelykende titrasie is gebaseer op die bepaling van alkaliniteit relatief tot 'n voorafbepaalde endpunt gebaseer op die veran= dering in kleur van 'n interne indikator. Daar is 'n aantal steurings geasso= sieer met laasgenoemde titrasieprosedure. Die natuurlike kleur of die ont= wikkeling van 'n presipitaat gedurende titrasie van die monster kan kleur= verandering van die interne indikator maskeer. Die teenwoordigheid van or= ganiese stowwe en veral die kleur wat daarmee geassosieer is, steur in die indikatormetode. Afvalmateriaal, wat in sommige waters voorkom, kan chemies steur deur die indikator te vernietig en varieerbare resultate mag voorkom met water wat oksiderende of reduserende stowwe bevat.

Weens die probleme wat ondervind word met die aansluiting van gemeganiseerde titrasieprosedures by vloei-analiseerders is hoofsaaklik beweeg na metodes wat gebaseer is op die verlies of verhoging in absorbansiewaardes in 'n aantal verskillende gebufferde suurbasis indikatoroplossings wanneer 'n watermonster hierby gevoeg word. Die analisefrekwens van die konvensionele geoutomatiseerde gesegmenteerde kontinue-vloeisisteem is egter net 60 monsters per uur.

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Willis en Mullins (1983) het twee instrumente geëvalueer om geskikte reaksietoestande te vind vir die bepaling van beide lae en hoë alkaliniteits= waardes volgens 'n konvensionele gesegmenteerde kontinue-vloei indikator= metode. Behalwe die lae analisefrekwens wat inherent is by gesegmenteerde vloei, het die outeurs ook probleme ondervind om die kalibrasiekromme oor die hele konsentrasiegebied te lineariseer. Van Staden en Van Vliet (1983) het 'n vinniger outomatiese prosedure vir die bepaling van totale alkaliniteit in oppervlakte-, grond- en huishoudelike water ontwikkel. Die metode is gebaseer op die beginsels van die vloei-inspuit tegniek gekombineer met die kolorimetriese bromokresolgroen bepaling en is geskik vir die analise van totale alkaliniteit teen 'n tempo van tot 120 monsters per uur met 'n variasie= koëffisiënt van beter as 1,40%. Daar is egter gevind dat die steurings soos hierbo genoem waaronder kleur, troebelrigheid en afvalmateriaal probleme veroorsaak wat hoofsaaklik bydra tot die lae akkuraatheid wat in sommige gevalle verkry word. Kleur en troebelrigheid kan verwyder word met die outomatiese voorklepfiltrasie met geaktiveerde koolstoffiltreerpapier wat deur Van Staden (1983) vir die vloei-inspuit turbidimetriese analise van sulfaat ont= wikkel is. Daar is egter gevind dat dit nie 'n oplossing bied vir die verwyde= ring van steurende oksiderende of reduserende stowwe wat in afvalwater voor= kom in die geval van die bepaling van totale alkaliniteit nie.

Hieruit blyk dit duidelik dat die akkuraatheid vir bogenoemde bepaling in vloeisisteme alleen verhoog kan word indien beweeg word na 'n prosedure wat gebaseer is op een of ander vorm van gemeganiseerde elektrometriese titrasies. Slegs 'n paar artikels oor kontinue-vloei titrators (Blaedel en Laessig (1964, 1965, 1966) het tot dusver verskyn. Die hoofnadeel van hierdie sisteme is die relatief lae analisefrekwens van ongeveer een monster elke ses minute.

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Ruzicka en medewerkers (1977) het die gradiënt idee by vloei-inspuit analise (VIA) aangepas in 'n verdere ontwikkeling van die kontinue titrimetriese tegniek. Die gradiënt is geskep binne-in 'n kontinue ongesegmenteerde vloeistroom. Die oorsprong van die gradiënt is teweeg gebring deur of 'n buis met 'n groter deursnee te gebruik of deur 'n miniatuur gradiëntkamer as deel van die vermengingsisteem te inkorporeer. Die tyd tussen die ekwivalente punte vir die stygende en dalende gedeelte van die titrasiekromme is eweredig aan die logaritme van die monsterkonsentrasie. Analisefrekwens is verhoog tot tussen 20 en 60 monsters per uur. Hierdie tegniek is verder verfyn deur Stewart (1981). Die nadele van hierdie sisteem is die volgende. Piekbreedte in plaas van piekhoogte word as meetsisteem gebruik. Omdat die breedte van die piek varieer, is dit moeilik om die tegniek te outomatiseer. Die breedste piek vorm die bepalende faktor en beheer dus die analisefrekwens. Die presisie van die metode is swak. In my laboratorium was die beste wat bereik kon word, 'n variasiekoëffisiënt van ongeveer 7%.

Die beste bydrae tot die meganisasie van titrasieprosedures op kontinue vloei-analiseerders is gelewer deur Åström (1979) wat die beginsel van enkelpunt titrasie (Leithe, 1964, Havas, 1975) met die vloei-inspuit tegniek gekombineer het. Enkelpunt titrasie is 'n intermediêre tegniek tussen direkte titrasie en direkte potensiometrie. Dit is algemeen bekend dat direkte titrasies nie uitgevoer kan word deur direkte pH metings nie, omdat probleme ontstaan met die onbekende dissosiasiegraad van die suur of basis wat bepaal word. Die rede hiervoor is die suur- of alkalifoute sowel as diffusiepotensiale wat ontstaan indien 'n glaselektrode gebruik word. Die grootte van die foutiewe verandering wat so sou ontstaan is 'n funksie van die samestelling van die monsters. Dit is wel moontlik om die invloed van hierdie faktore tot 'n mate te elimineer, maar die probleem dat die verband tussen pH en

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hidroksonium ioonaktiwiteit logaritmies is, bly voortbestaan.

Dit is egter wel moontlik om al die genoemde faktore te vermy. Verder kan die pH-konsentrasieverband gelineariseer word deur die toepassing van konstante ioonsterkte, lineêre-respons reagense. Hierdie reagense bestaan uit 'n mengsel van swak sure of swak basisse. Gebruik van hierdie reagense voorsien feitlik 'n lineêre verband tussen die hoeveelheid basis of suur in die monster en die pH. Met die toepassing van hierdie reagense, kan gewone titrasies as oortollig en stadig beskou word. Sure en basisse kan op 'n eenvoudige en vinniger wyse bepaal word deur 'n enkele pH-meting. 'n Metode vir die berekening van die samestelling van hierdie reagense en 'n evaluering van die voorbereide mengsels word gegee deur Johansson en Backen (1974).

Åström (1979) het die beginsel van lineêre respons reagense en vloei-inspuit analise gekombineer deur 'n prosedure vir enkelpunt vloei-inspuit titrasies te beskryf wat toegepas word op die analise van sure en basisse, asook mengsels daarvan. Die invloed van monstergrootte, dispersie, lynlengte en vloeitempo is ondersoek. Daar is gevind dat piekmaksima 'n lineêre funksie van die suur-basis konsentrasie in die gebied 0,01 tot 0,1 $mol \cdot dm^{-3}$ vir monoprotiese en monobasiese sisteme is teen 'n monsternemingstempo van 180 monsters per uur met die relatief standaardafwyking van beter as 1%.

Die toepasbaarheid van bogenoemde beginsel op die komplekse karbonaatsisteem is ondersoek. Hierdie artikel beskryf die resultate van so 'n ondersoek en die praktiese uitvoerbaarheid daarvan as 'n vloei-inspuitprosedure vir die bepaling van totale alkaliniteit in oppervlakte-, grond- en huishoudelike water.

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EKSPERIMENTEEL

Apparaat

(i) Monsternemingsklep

'n Carle mikrovolume tweeposisie monsternemingsklep (Carle Katalogusnommer 2014) met twee monsternemingslusse is gebruik. Die klepsisteem is gesinchroniseer met die monsternemingseenheid. 'n Peristaltiese pomp voorsien die draerstroom teen 'n konstante vloeitempo.

(ii) Cenco monsternemer

(iii) Cenco peristaltiese pomp wat teen 10 revolusies per minuut funksioneer.

(iv) Vermengingsisteem (kyk Figuur 2).

(v) Orion model 901 pH meter.

(vi) Schott mikro pH gekombineerde elektrode met tipe N60 silindriese glasmembraan, Ag/AgCl interne verwysingselemente, zero potensiaal pH-waarde = 7, platinum aansluiting, weerstand (R) by 25°C = 600 MΩ, deursnee 3 mm en werkgebied 20 tot 80°C en pH 0 tot 14.

(vii) Cenco registreerder.

Reagense

Analities reagens graad reagense is gebruik, tensy dit ander gespesifiseer is.

(i) Natriumchloriedoplossing

Los 11,688 g natriumchloried in gedistilleerde water op en verdun kwantitatief na 2 dm^3. Dit lewer 'n 0,10 $mol \cdot dm^{-3}$ NaCl-oplossing.

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(ii) Stam-bufferoplossing

Berei 'n mengsel wat bestaan uit die volgende bufferkomponente. Los elkeen agtereenvolgens soos hieronder aangedui op in 4 dm^3 van 'n 0,10 $mol \cdot dm^{-3}$ NaCl-oplossing en verdun kwantitatief na 5 dm^3 met 'n 0,10 $mol \cdot dm^{-3}$ NaCl-oplossing.

(a) 1,1135 g soutsuur

(b) 0,8300 g diëtielmalonaat

(c) 42,0980 g sitroensuur

(d) 2,5370 g p-nitrofenol

(e) 31,9310 g diëtielbarbituursuur

(f) 14,7010 g boorsuur

Die samestelling van hierdie mengsel is krities.

(iii) Werkbufferoplossings

Verdun die stam-bufferoplossing tienkeer met 'n 0,10 $mol \cdot dm^{-3}$ NaCl-oplossing. Neem 100 cm^3 van die stamoplossing en verdun kwantitatief na 1 dm^3 met 'n 0,10 $mol \cdot dm^{-3}$ NaCl-oplossing.

(iv) 0,1 $mol \cdot dm^{-3}$ NaOH-oplossing

Los 4 g natriumhidroksied op en verdun kwantitatief na 1 dm^3 met gedistilleerde water. Berg die oplossing in 'n poli-etileenhouer.

(v) 0,1 $mol \cdot dm^{-3}$ soutsuuroplossing

Los 8 cm^3 gekonsentreerde soutsuur (soortlike gewig = 1,19; pro analysi-Merck) in 500 cm^3 gedistilleerde water op. Verdun kwantitatief na 1 dm^3 met gedistilleerde water.

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Standaarde

(i) Stam-waterstofkarbonaatoplossing

Los 13,7678 g natriumwaterstofkarbonaat ($NaHCO_3$), gedroog vir 1 uur by 60°C, in gedistilleerde water op. Verdun kwantitatief na 1 dm^3 met gedistilleerde water. Hierdie oplossing bevat 10 mg waterstofkarbonaatione in 1 cm^3.

(ii) Standaard-waterstofkarbonaatwerkoplossings

Berei die volgende reeks standaard werkoplossings in 500 cm^3 volumetriese flesse.

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Nommer	Volume stamoplossing (cm^3)	Waterstofkarbonaat ioonkonsentrasie ($mg \cdot dm^{-3}$)
1	1,0	20
2	2,0	40
3	3,0	60
4	4,0	80
5	5,0	100
6	7,5	150
7	10,0	200
8	12,5	250
9	15,0	300
10	17,5	350
11	20,0	400
12	22,5	450
13	25,0	500
14	27,5	550
15	30,0	600
16	32,5	650
17	35,0	700
18	37,5	750
19	40,0	800

Monsterpreservering

Preserveer die monsters met 20 mg Hg(II) per dm^3 monster. Die monsterbottels moet heeltemal gevul wees en moet nie voor die analise oopgemaak word nie.

ANALITIESE VLOEISISTEEM

'n Skematiese diagram van die analitiese vloeisisteem vir die bepaling van totale alkaliniteit verskyn in Figuur 2. Die vermengingsisteem bestaan uit Tygonbuise met 'n binnedeursnee van 0,51 mm. Die buise is as vermengingspoele om 15 mm perspexstawe gedraai. Lynlengtes word in Figuur 2 aangetoon. 'n Cenco peristaltiese pomp wat teen 10 revolusies per minuut funksioneer voorsien die draer en bufferstrome teen konstante vloeitempo's. Monsters van 'n outo= matiese Cenco monsternemer word outomaties met behulp van 'n 28 µℓ monsterlus in die draerstroom ingelaat. 'n 30 Sekonde monstersiklus word tussen opeenvolgende monsters gehandhaaf. Dit gee 'n analisefrekwens van 120 monsters per uur. Die monsternemingsklepsisteem skakel elke 28 sekondes nadat die monsternemer na die volgende monster beweeg het. Die klepsisteem is gesinchroniseer met die monsternemingseenheid.

Die analitiese vloeisisteem word, nadat die werksvrag monsteranalises voltooi is, eers vir 10 minute met 0,1 $mol \cdot dm^{-3}$ NaOH-oplossing, dan vir 10 min. met 0,1 $mol \cdot dm^{-3}$ HCl-oplossing en finaal vir 10 minute met water gespoel. Dit is nodig omdat die buffermengsel tesame met die NaCl-oplossing 'n neerslag in die buisies mag vorm wanneer dit oornag staan.

RESULTATE EN BESPREKING

In die bepaling van totale alkaliniteit in water met vloei-inspuit analise beïnvloed die bufferkapasiteit van die vloeistroom in die deurvloeidetektor die lineariteit van die bepaling. Die bufferkapasiteit is 'n funksie van die bufferkonsentrasie. Die bufferkonsentrasie in die omgewing van die deurvloei= detektor word deur die draerstroomvloeitempo, bufferstroomvloeitempo en die

reagensbottel se bufferkonsentrasie beheer. Gevolglik is daar besluit om eers die konsentrasies van die verskillende komponente in die bufferoplossing wat in die reagensbottel teenwoordig is te optimiseer.

Johansson en Backen (1974) het gevind dat dit moontlik is om 'n mengsel van swak sure te berei wat feitlik 'n lineêre verband tussen die hoeveelheid basis in die monster en die pH verskaf vir eenvoudige sisteme. Samevattend kom dit kortliks op die volgende neer. 'n Deel van die titrasiekromme van 'n swak suur teen 'n sterk basis is lineêr soos aangetoon in Figuur 3. Soortgelyk sal die titrasiekromme van 'n mengsel van swak sure teen 'n sterk basis gedeeltelik lineêr wees. Vanuit laasgenoemde kromme is dit moontlik om die hoeveelheid basis in 'n monster grafies te bepaal. Eksperimenteel impliseer dit die byvoeging van 'n monster by 'n mengsel van die sure en die aflees van die pH vanuit die kromme. Indien die kalibrasiekromme meer gelineariseer kan word tot 'n reguit lyn, sal evaluering van die resultate verder vereenvoudig. Die eerste stap in hierdie proses was om 'n verband tussen die konsentrasie van 'n basis, b, en die pH (of die waterstofioonkonsentrasie) in 'n gemengde oplossing te herlei. Dit is die omgekeerde van die berekening van pH in 'n mengsel van swak sure en 'n sterk basis. Vir 'n dibasiese suur, H_2A, kan die volgende toestande neergeskryf word.

$$b + [H^+] = [OH^-] + [HA^-] + 2\,[A^{2-}] \qquad \text{----- (1)}$$

$$A_{tot} = [H_2A] + [HA^-] + [A^{2-}] \qquad \text{----- (2)}$$

$$[HA^-] = K_1[H_2A]/[H^+] \qquad \text{----- (3)}$$

$$[A^{2-}] = K_1K_2[H_2A]/[H^+]^2 \qquad \text{----- (4)}$$

$$[OH^-] = K_w/[H^+] \qquad \text{----- (5)}$$

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Vergelykings (3) en (4) is alleen geldig indien die ioonsterkte konstant gehou word. Die beste akkuraatheid kan verkry word indien die beskikbare pH gebied gelykmatig bedek word met swak sure sodat die verband tussen pH en b 'n reguit lyn is. Die verband kan beskryf word deur die vergelyking

$$pH = k \cdot c + \ell$$

waar ℓ die snypunt op die pH-as is indien geen basis bygevoeg is nie, k is die helling van die lyn en c is 'n basisveranderlike vir 'n wiskundige lineêre geval. Soos gesien kan word uit die vergelyking is k die inversie van β die bufferkapasiteit, sodat 'n mengsel wat hierdie verband aantoon 'n konstante bufferwaarde oor 'n sekere pH-gebied handhaaf. Indien k verander, verander die bufferkapasiteit. Die helling en die snypunt op die pH-as word arbitrêr gekies. Die verband tussen c en b (Johansson en Backen, 1974) word in Figuur 4 aangetoon. Johansson en Backen het van matriksalgebra gebruik gemaak waar integrasie van die elemente uitgevoer is oor die pH-gebied waar linearisasie verlang word.

Deur van die teoretiese aanvoorwerk van Johansson en Backen (1974) gebruik te maak, was Åström (1977, 1978, 1979) in staat om 'n rekenaarprogram in FORTRAN te ontwikkel vir die evaluering en berekening van die individuele suurkonsentrasies in so 'n mengsel sodat 'n teoretiese lineêre titrasiekromme verkry kon word. Die program is eksperimenteel deur Åström aangewend vir die eksperimentele bepaling van eenvoudige suur-basissisteme met behulp van enkelpunttitrasies. Die outeurs (Johansson en Backen, 1974; Åström, 1977, 1978, 1979) het egter gevind dat daar sekere kriteria is waaraan so 'n suur=mengsel sowel as die eksperimentele prosedure moet voldoen voor die sukses=volle implementering in 'n enkelpunttitrasie. Van die belangrikste vereistes is dat

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(i) die reagens 'n hoë inerte elektrolietkonsentrasie moet bevat

(ii) die suurmengsel aan so min syreaksies (kompleksvorming, presipitasie en redoksreaksies) as moontlik onderworpe moet wees

(iii) alle basisse volledig geprotoneer moet kan word.

Daar is gevind dat veral die laaste twee vereistes probleme skep by die linearisering van so 'n titrasiekromme vir die komplekse karbonaatsisteem. Die kompleksiteit van die karbonaatsisteem blyk duidelik uit Figuur 5 waar die verband tussen die alkaliniteit- en asiditeittitrasieskrommes sowel as die ooreenstemmende pC-pH-diagram aangedui word. Daar is gevind dat die direkte toepassing van die Åström-sisteme nie op die komplekse karbonaatsisteem funksioneer nie. Met die kompleksiteit van die karbonaatsisteem in sy totaliteit in ag geneem, is die volgende werkswyse gevolg by die optimisering van die konsentrasies van die verskillende komponente in die buffersisteem.

Die eerste stap was om die rekenaarprogram in FORTRAN wat van Åström (1977) ontvang is aan te pas by die IBM 4341 stelsel wat by die Universiteit van Pretoria in gebruik is. Tweedens moes die kompleksiteit van die karbonaatsisteem in ag geneem word. Omdat die karbonaatsisteem wesentlik 'n ewewigsisteem van verskeie swaksuur-swakbasissisteme is, was die korrekte keuse van die verskillende komponente van die buffersisteem 'n kritiese faktor. Dit was nodig om die verskillende komponente sodanig te evalueer en te optimiseer dat newereaksies tot 'n minimum beperk word, die hoofreaksie-ewewig voldoende plaasvind sodat 'n realistiese meetbare gevoeligheid verkry kon word wat ook gepaard sou gaan met lineariteit.

Åström (1978, 1979) het aangetoon dat indien die lineêre bufferoplossing vir enkelpunttitrasie verdun word, die verband tussen konsentrasie en pH steeds

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lineêr bly en dus steeds analities gebruik kon word, alhoewel die oor=spronklike helling nie behoue bly nie. Voorlopige eksperimente het aange=toon dat dit nie geld in die bepaling van totale alkaliniteit nie.

Met al bogenoemde faktore in ag geneem, is verskeie buffersisteme geëvalueer en ge-optimiseer totdat 'n geskikte buffersamestelling gevind is.

Vir die enkelpunttitrasie van die alkaliniteitsmonster met die lineêre buffermengsel, word 'n sekere reaksietydsverloop benodig om reaksie-ewewig te bereik en is 'n sekere graad van vermenging nodig vir hoë presisie. Deur die totale dispersie van die ingespuite monstersone te beheer, kon aan boge=noemde vereistes voldoen word. Dit is verkry deur die evaluering en optimisering van die lynlengtes, buisdeursnee, draerstroom- en bufferstroomvloeitempo's asook die verhouding van die draerstroom- tot bufferstroomvloeitempo's en monstervolume. Verdunning van die buffermengsel het ook 'n belangrike bydrae gelewer by die optimisering van bogenoemde parameters. Bogenoemde parameters is egter almal interafhanklik, gevolglik moes 'n tipe van simpleksoptimisering by die voorlopige evaluering toegepas word. Lynlengte, buisdeursnee en draer=stroomvloeitempo beïnvloed nie net die presisie en lineariteit nie, maar ook die analisefrekwens van die bepaling. Daar is gevind dat 'n buisdeursnee van 0,51 mm en 'n lynlengte van 250 cm die beste resultate lewer ten opsigte van presisie en analisefrekwens. Resultate het verder getoon dat 'n draerstroom=vloeitempo van 3,9 $cm^3 \cdot min^{-1}$ en 'n bufferstroomvloeitempo van 0,8 $cm^3 \cdot min^{-1}$ die beste kontinue verdunning, analisefrekwens, lineariteit en presisie lewer. Indien die verhouding tussen die draerstroom- en bufferstroomvloeitempo vergroot word, lei dit effektief tot 'n groter verdunning van die buffermengsel in die vermengingsisteem. Gevolglik neem die gevoeligheid van die sisteem toe, maar die lineariteit van die kalibrasiekromme verswak drasties.

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Verdere verhoging van die draerstroomvloeitempo verlaag die presisie, terwyl drukprobleme in die buise ontstaan wat gepaard gaan met lekkasies wat ontstaan en buise wat afspring. Dienooreenkomstig neem die gevoeligheid van die sisteem af indien die verhouding tussen draerstroom- en bufferstroom= vloeitempo's verklein word. Terselfdertyd neem die analisefrekwens af indien die draerstroomvloeitempo verlaag word.

Monstervolume en verdunning van die oorspronklike bufferkonsentrasie (soos teoreties bereken vir elke individuele komponent van die mengsel) beïnvloed ook lineariteit en presisie. In die geval van lineariteit is gevind dat die monstervolume en verdunning interafhanklik en 'n kritiese faktor is. Gevolglik is die invloed van verdunning op monstervolume ondersoek. Dit is herhaal vir 'n paar monstervolumes. Die resultate verskyn in Figure 6, 7, 8, 9 en 10. Die verdunnings wat in die verskillende figure gebruik is, is verdunning van die konsentrasie van die buffersisteem soos oorspronklik teoreties bereken is. Uit die figure blyk die volgende algemene tendense duidelik. Die vloei-inspuit analitiese titrasiekromme is nêrens heeltemal lineêr nie. Die lineariteit verswak met toenemende verdunning. Verder word gevind dat die bufferkapasiteit vir die hoë alkaliniteitswaardes nie voldoende is by verdunnings vanaf 1:40 tot 1:80 nie, veral vir monstervolumes van 46 µℓ en 70 µℓ. By 24 µℓ is die gevoeligheid van die sisteem vir die beste lineêre titrasiekromme (1:40 verdunning) baie laag sodat die presisie verswak. By 46 µℓ en 70 µℓ is die presisie ook swak vanweë die lengte en straal van die monsterskyf wat in die sisteem ingespuit word. Monsteroordrag kom ook voor. Dit is ook duidelik dat die lineariteit wat aanvanklik swak is, baie afneem met toenemende verdunning, veral by die lae en hoë alkaliniteits= waardes. Daar is gevind dat 'n monstervolume van 28 µℓ en 'n verdunning van 1:20 van die oorspronklike buffermengsel die beste lineariteit, presisie en

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analisefrekwens lewer. (Vir die stam-bufferoplossing soos dit onder eksperi=menteel uiteengesit is, is dit 'n tienvoudige verdunning).

Die resultate van 'n reeks totale alkaliniteit standaardoplossings, vier=voudig elk ge-analiseer, verskyn as 'n tipiese verteenwoordigende strookkaart registreerderuitdruk in Figuur 11. Die analisetempo is 120 monsters per uur. Die uittreësein van die pH-meter word op 'n tweepen-registreerder in twee verdeel sodat hoë sowel as lae totale alkaliniteitswaardes met dieselfde vloei-inspuitsisteem terselfdertyd bepaal kan word. Die 10 mV-instelling van die registreerder word vir lae totale alkaliniteitswaardes (0 tot 300 $mg \cdot dm^{-3}$ waterstofkarbonaat) gebruik, terwyl die 20 mV-instelling vir die hoë waardes (300 tot 800 $mg \cdot dm^{-3}$ waterstofkarbonaat) geskik is. 'n Kalibrasie=kromme, wat beide gebiede aantoon, verskyn in Figuur 12.

Die invloed van monsteroordrag is geëvalueer deur analises na willekeur uit te voer (kyk Figuur 13). Dit blyk duidelik dat die oordrag van een monster na 'n tweede minimaal is (kleiner as 0,5%). Geen noemenswaardige basislyndryf vir die meer as 160 bepalings (oor 'n tydperk van langer as 1 uur) soos aangetoon in Figuur 13 is ondervind nie.

Die presisie van die metode is op standaarde (Tabel 1) en op standaardmonsters getoets (Tabel 2). Die standaardafwyking is minder as 0,8% vir 16 toetse op elke watermonster.

Om die akkuraatheid van die voorgestelde VIA-metode te toets, is 'n reeks monsters ge-analiseer en die resultate vergelyk met dié wat verkry is met die elektrometriese metode (Standard Methods for the Examination of Water and Wastewater, 1980; - American Society for Testing an Materials, 1975) en

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'n outomatiese bromokresolindikatormetode. Die voorgestelde VIA-metode vergelyk verder gunstig met 'n standaard elektrometriese metode en in sommige gevalle is beter resultate verkry met die standaard elektrometriese metode as wat die geval met die bromokresolmetode was. (Kyk Tabel 2). Dit is moontlik weens steurings alreeds genoem (byvoorbeeld kleursteurings) wat in die monsters aanwesig mag wees. Die akkuraatheid van die voorgestelde metode is ook getoets deur die standaard addissiemetode. Bekende hoeveelhede totale alkaliniteit is by watermonsters gevoeg en die resultate voor en na addissie is verwerk. Die waardes wat verkry is deur die voorgestelde metode en deur die standaard addissiemodifikasie verskyn in Tabel 3. Dit blyk duidelik dat die herwinbaarheid voldoende is. Die herwinbaarheid van die voorgestelde metode oor vyf dae is ook getoets. Kontrole monsters is oor 'n tydperk van vyf dae teen standaardoplossings geëvalueer. Herwinbaarheid was beter as 99%. Die resultate het egter getoon dat die waardes van sommige monsters wel betekenisvol kan wissel indien die monsterbottels te veel oop= gelaat en aan die atmosfeer blootgestel word.

SLOTSOM

Die VIA-metode wat hier beskryf word, is geskik vir die bepaling van totale alkaliniteit teen 'n tempo van 120 monsters per uur met 'n variasiekoëffisiënt van beter as 0,8%.

ERKENNING

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TABEL 1

Resultate van die presisietoets vir die voorgestelde VIA metode soos uitgevoer op 'n reeks standaardoplossings

Monster	Waterstofkarbonaatkonsentrasie as $mg \cdot dm^{-3}$	Standaard= [a] afwyking %
1	20	0,79
2	40	0,77
3	60	0,76
4	80	0,74
5	100	0,73
6	150	0,70
7	200	0,70
8	250	0,68
9	300	0,67
10	350	0,61
11	400	0,57
12	450	0,56
13	500	0,54
14	550	0,52
15	600	0,47
16	650	0,44
17	700	0,38
18	750	0,32
19	800	0,29

[a]Vir 16 toetse in elke geval.

VIA = vloei-inspuitanalise

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TABEL 2

Vergelykking van resultate verkry met 'n standaard outomatiese gesegmenteerde metode, die elektrometriese metode en die voorgestelde VIA-metode.

Monster	Outomatiese gesegmenteerde metode $[HCO_3^-]$ in $mg \cdot dm^{-3}$	Elektrometriese metode $[HCO_3^-]$ in $mg \cdot dm^{-3}$	VIA-metode $[HCO_3^-]$ in $mg \cdot dm^{-3}$	Standaard= [a] afwyking %
1	27	27	27	0,78
2	7	8	8	0,80
3	6	9	8	0,80
4	15	16	16	0,79
5	13	14	14	0,82
6	9	11	12	0,79
7	57	61	62	0,75
8	61	64	68	0,74
9	31	30	29	0,77
10	39	36	37	0,76
11	59	128	136	0,71
12	79	137	148	0,69
13	122	151	160	0,70
14	34	37	38	0,76
15	105	121	124	0,72
16	158	199	196	0,70
17	189	237	242	0,66
18	58	64	62	0,76
19	264	281	276	0,67
20	462	489	499	0,54
21	46	53	48	0,76
22	267	291	288	0,69
23	41	41	42	0,76
24	421	435	432	0,57
25	357	344	348	0,60
26	49	46	48	0,77
27	295	291	296	0,66
28	671	644	637	0,45
29	465	497	490	0,53
30	48	48	48	0,77

[a]Gemiddelde resultaat van 16 toetse in elke geval

VIA = vloei-inspuitanalise

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TABEL 3

Vergelyking van resultate verkry met die voorgestelde VIA-metode sonder en met die standaard addissiemetode.

Monster	VIA sonder standaard addissie	VIA met standaard addissie	Herwinbaarheid (%)
1	48	47	97,9
2	27	27	100,0
3	490	486	99,2
4	637	631	99,1
5	348	354	101,7
6	276	272	98,6
7	160	159	99,4
8	196	189	96,4
9	62	61	98,4
10	37	38	102,7

VIA = vloei-inspuitanalise

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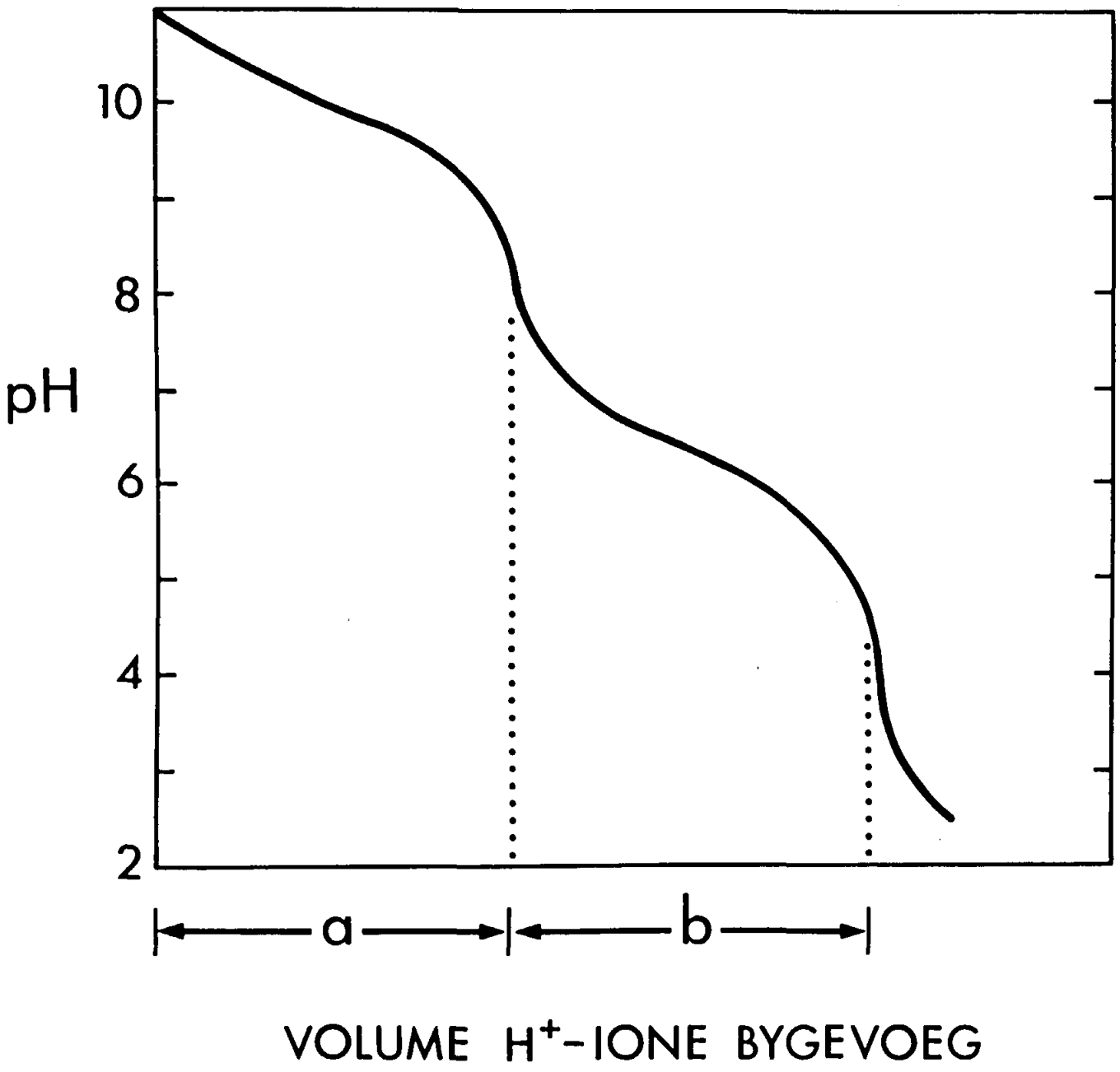
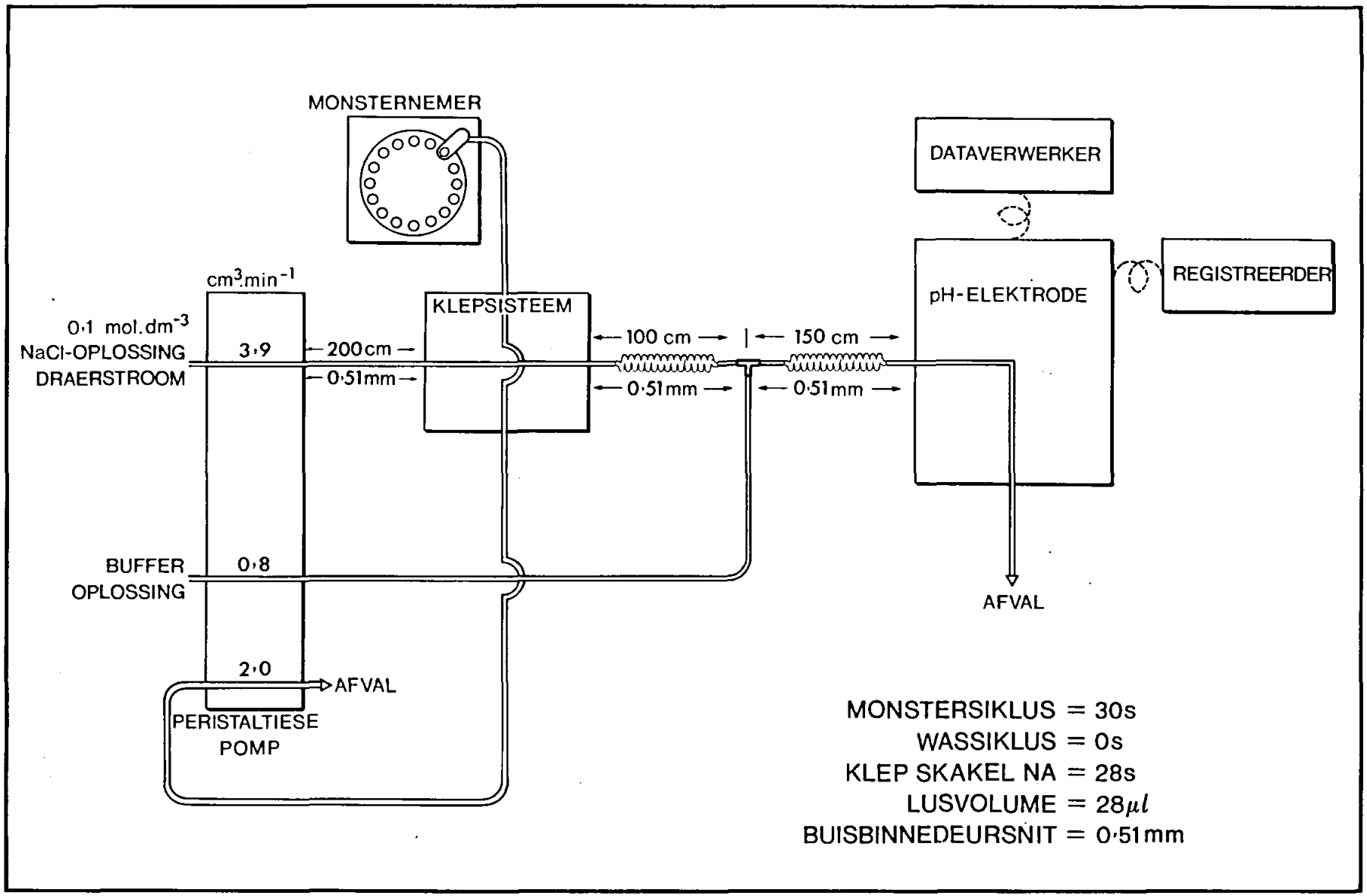
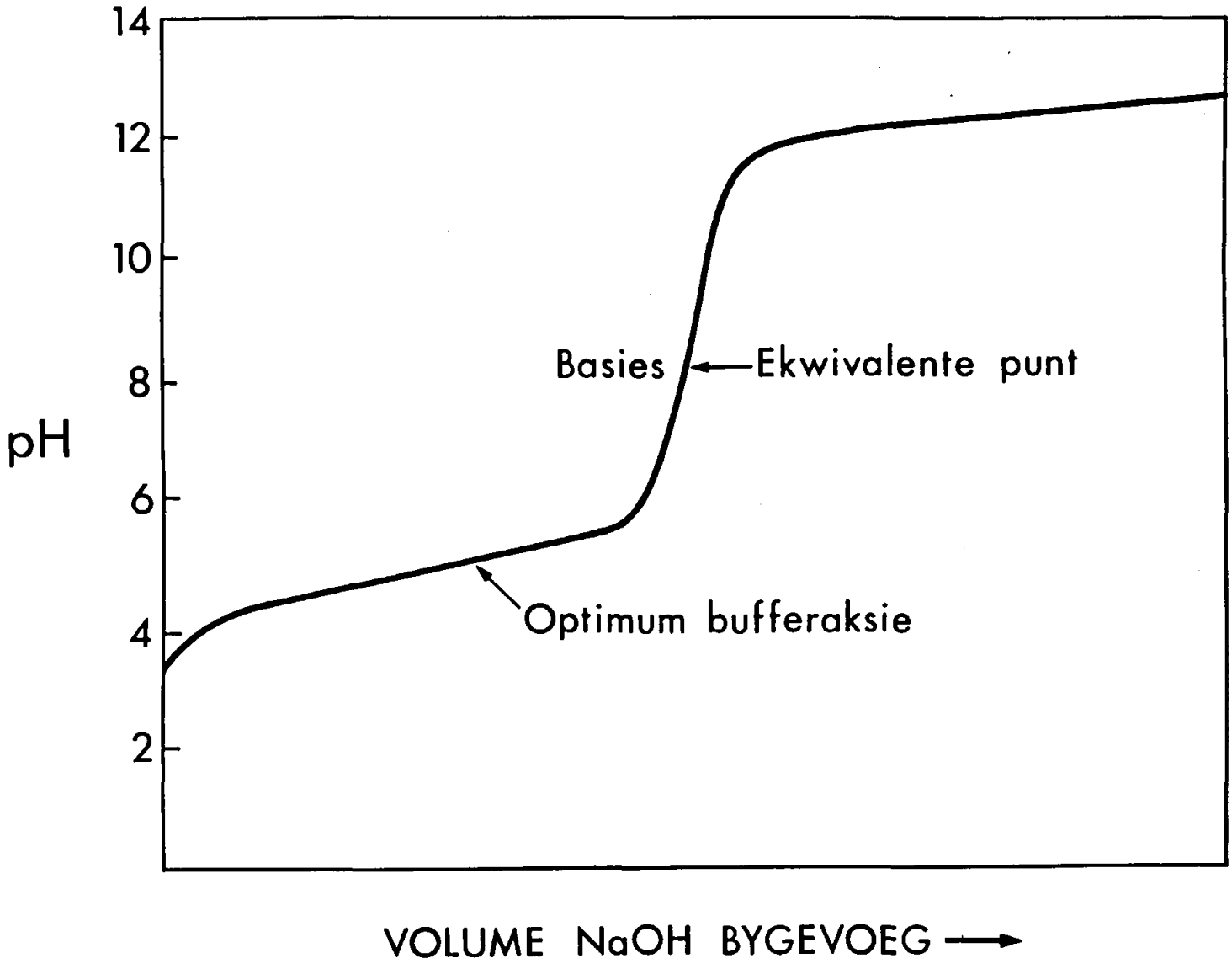


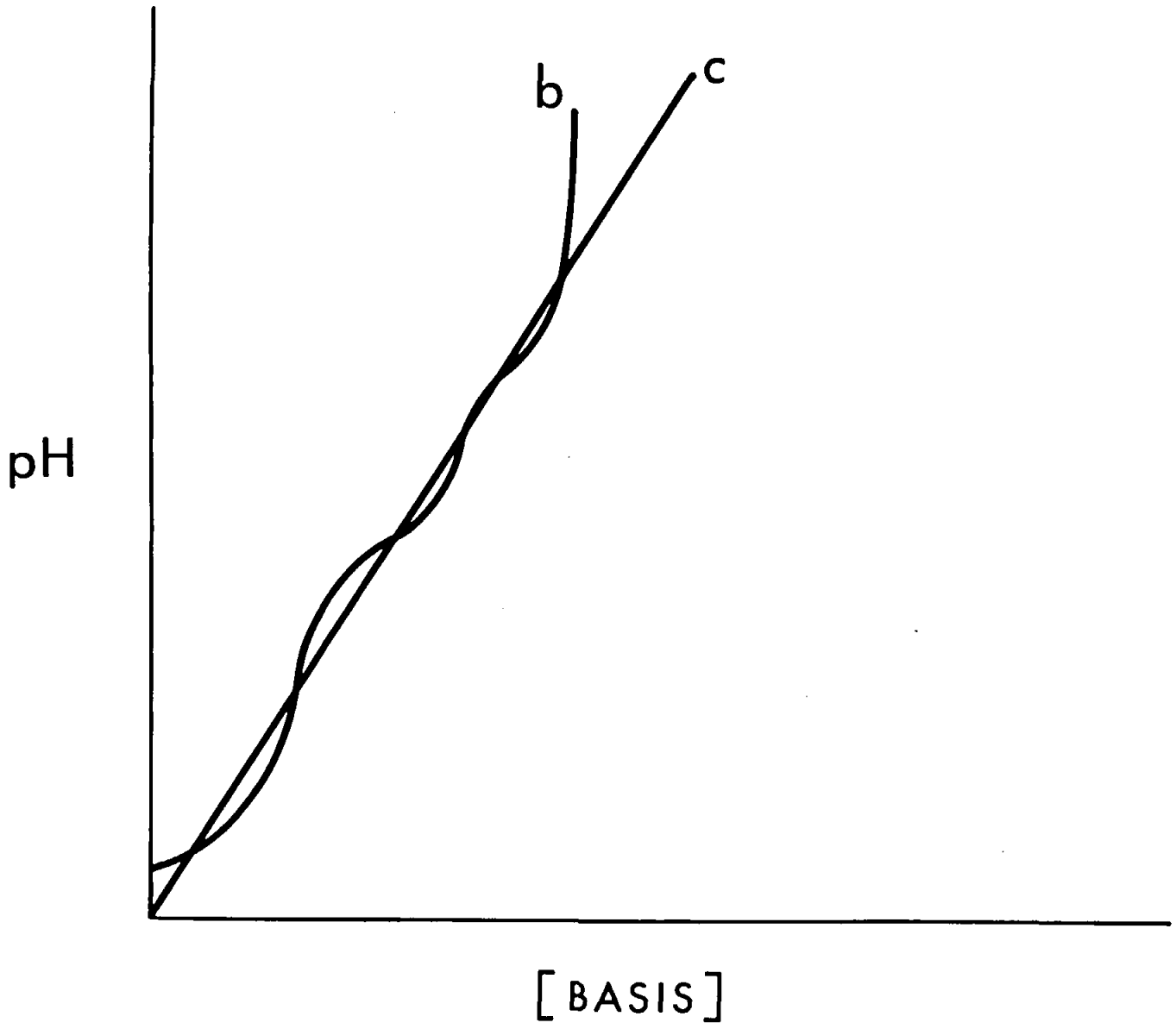
Figuur 1. Alkaliniteittitrasiekromme. Gebied a dui die hoeveelheid H^+-ione aan wat nodig is om die OH^--ione te neutraliseer en CO_3^{2-}- na HCO^--ione om te skakel. Gebied b dui die hoeveelheid H^+-ione aan wat nodig is om HCO_3^--ione na H_2CO_3 om te skakel.



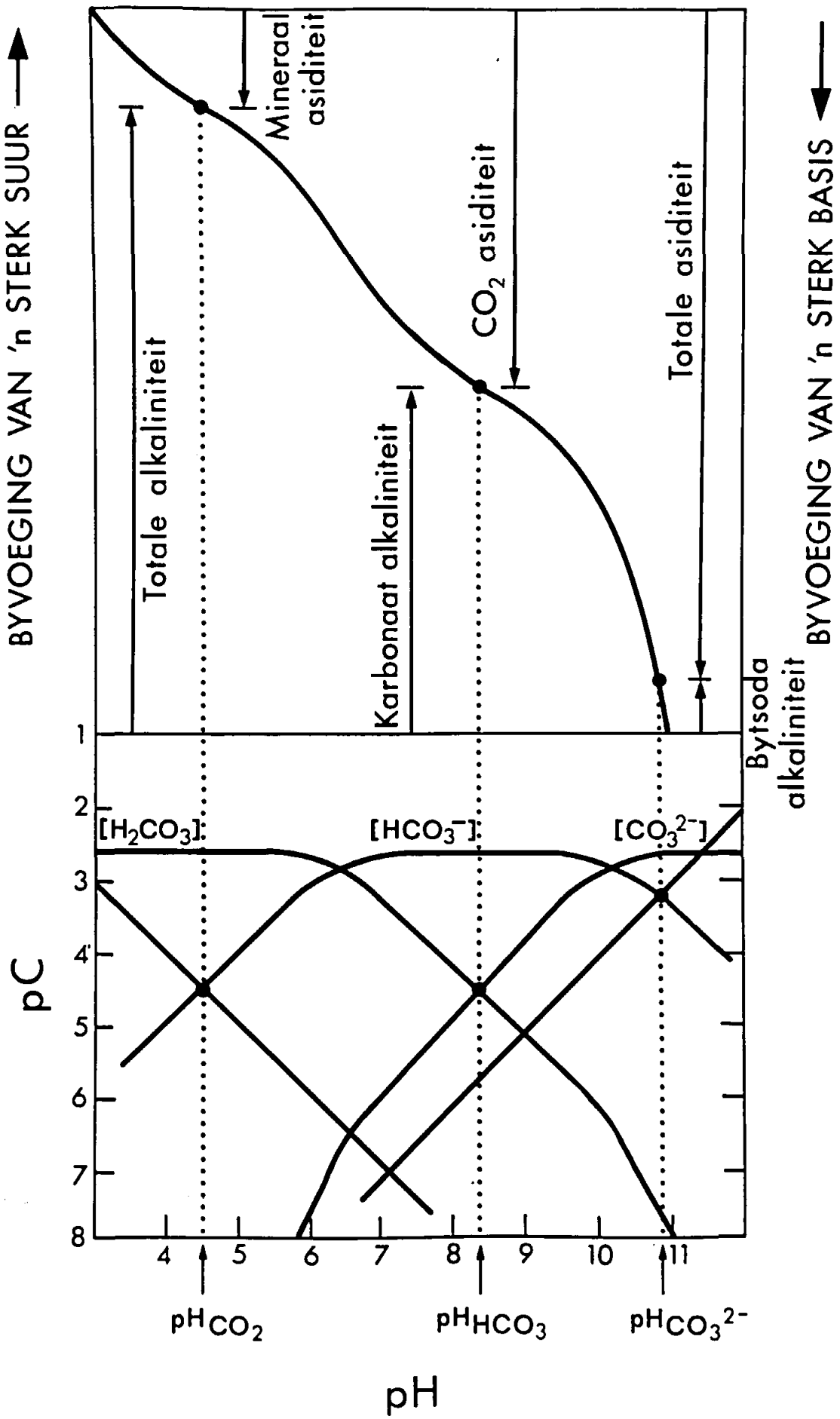
Figuur 2. Vloeidiagram vir totale alkaliniteit. Analisefrekwens 120 monsters per uur. Buislengte en -binnedeursnit word respektiewelik in cm en mm gegee.



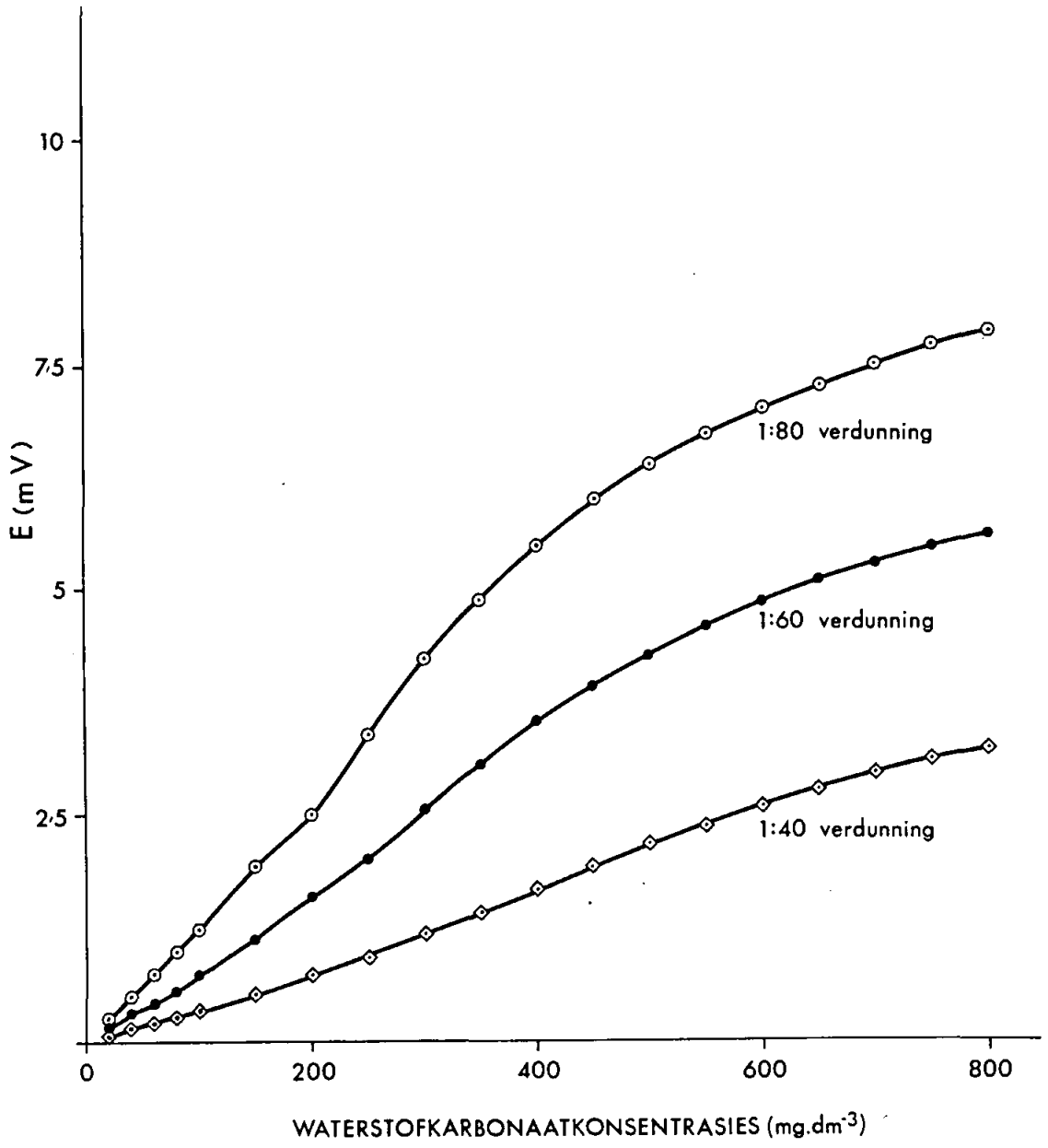
Figuur 3. Titrasiekromme vir die titrasie van 'n swak monoprotiese suur met 'n sterk basis.



Figuur 4. Die verband tussen 'n wiskundig berekende lineêre veranderlike c en 'n eksperimenteel fisies verkrygbare veranderlike b.



Figuur 5. Verband tussen die pC-pH-diagram en die titrasie-kromme vir die karbonaatsisteem by 25°C.



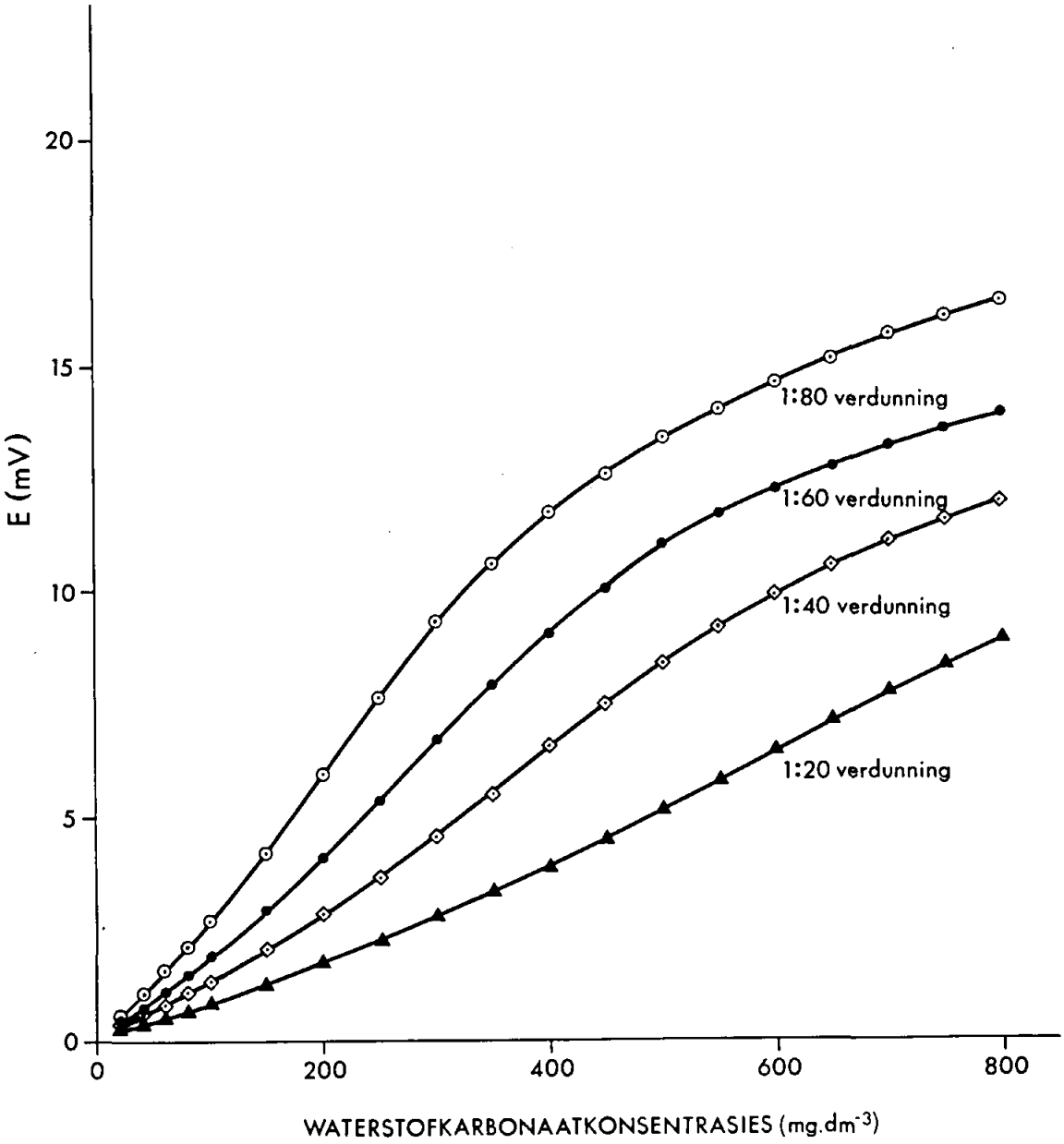
Figuur 6. Invloed van monstervolume en verdunning op lineariteit.

Monstervolume = 24 µℓ

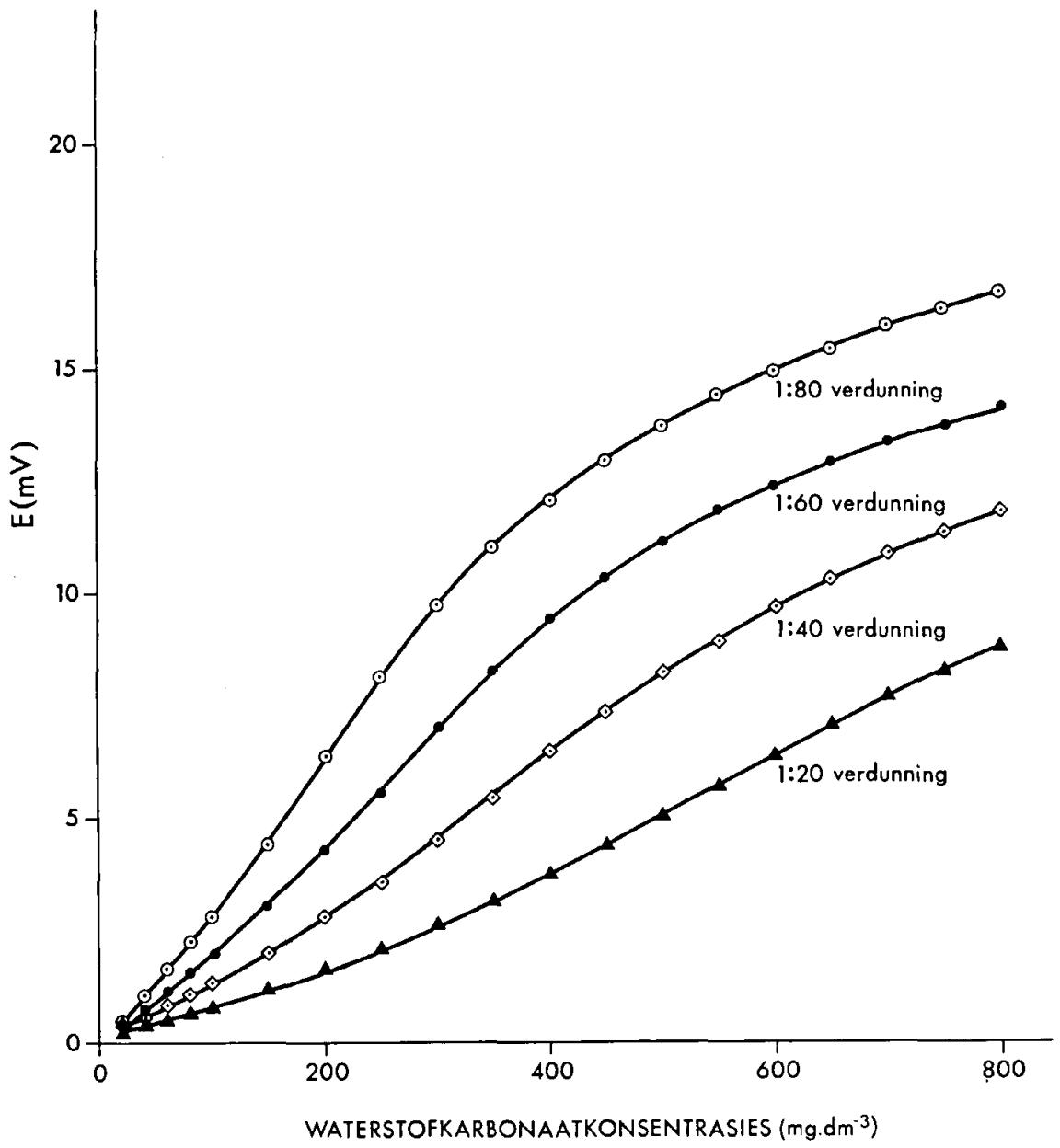
Draerstroomvloeitempo = 3,90 $cm^3 \cdot min^{-1}$

Bufferstroomvloeitempo = 0,80 $cm^3 \cdot min^{-1}$

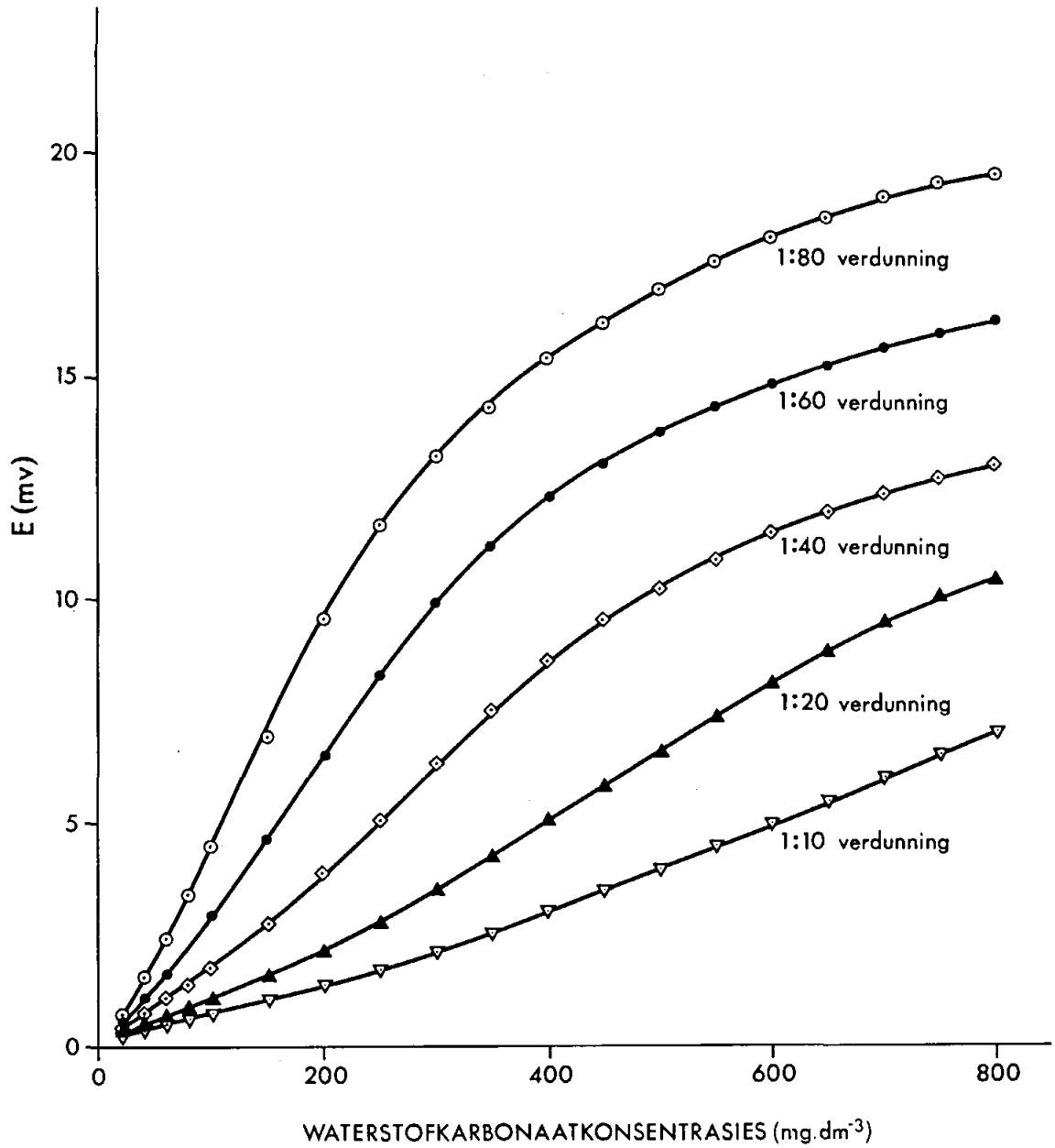
Lynlengte = 250 cm. Buisdeursnee = 0,51 mm.



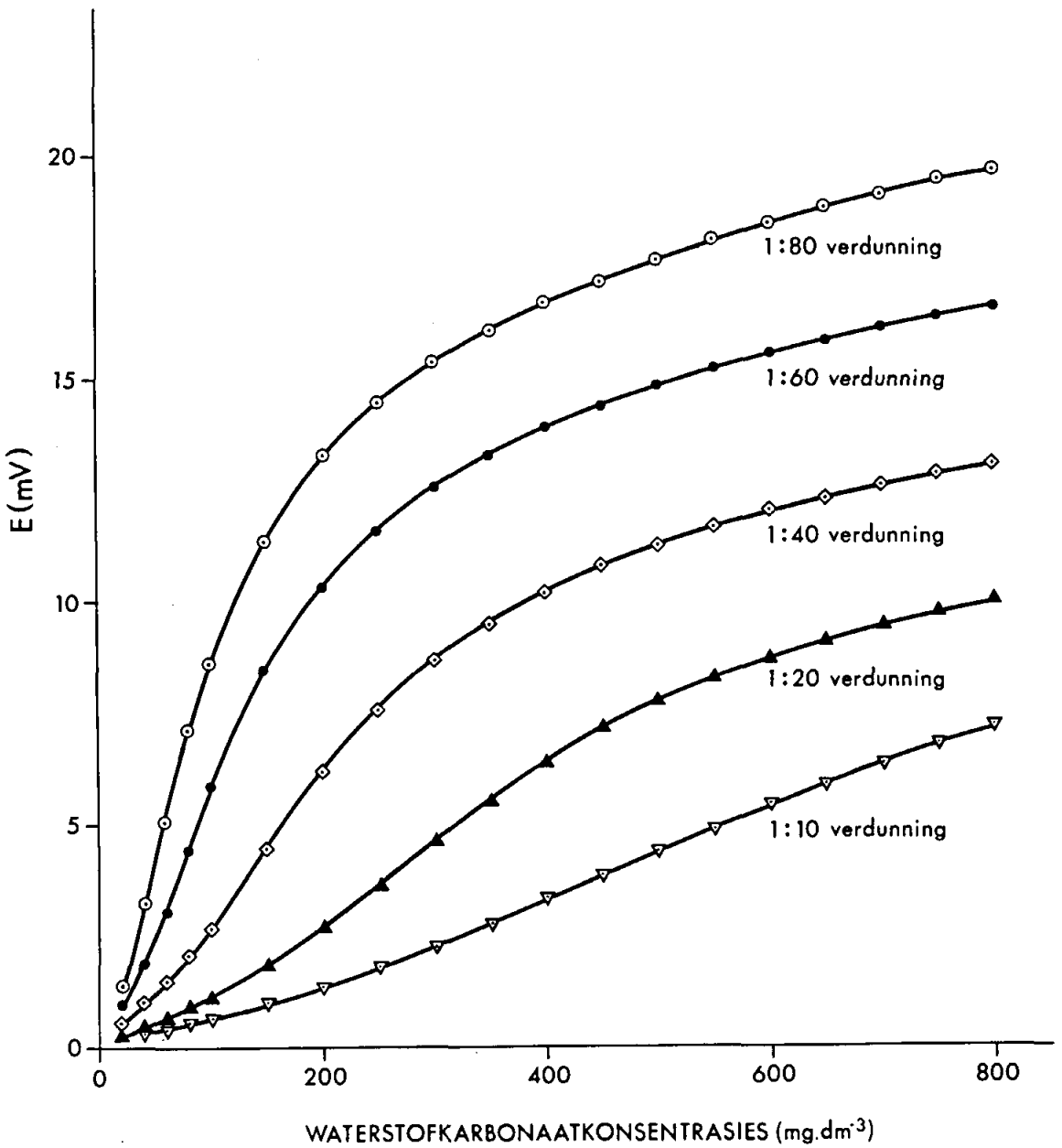
Figuur 7. Invloed van monstervolume en verdunning op lineariteit Monstervolume = 28 µℓ. Draerstroomvloeitempo = 3,90 $cm^3 \cdot min^{-1}$. Bufferstroomvloeitempo = 0,80 $cm^3 \cdot min^{-1}$. Lynlengte = 250 cm. Buisdeursnee = 0,51 mm.



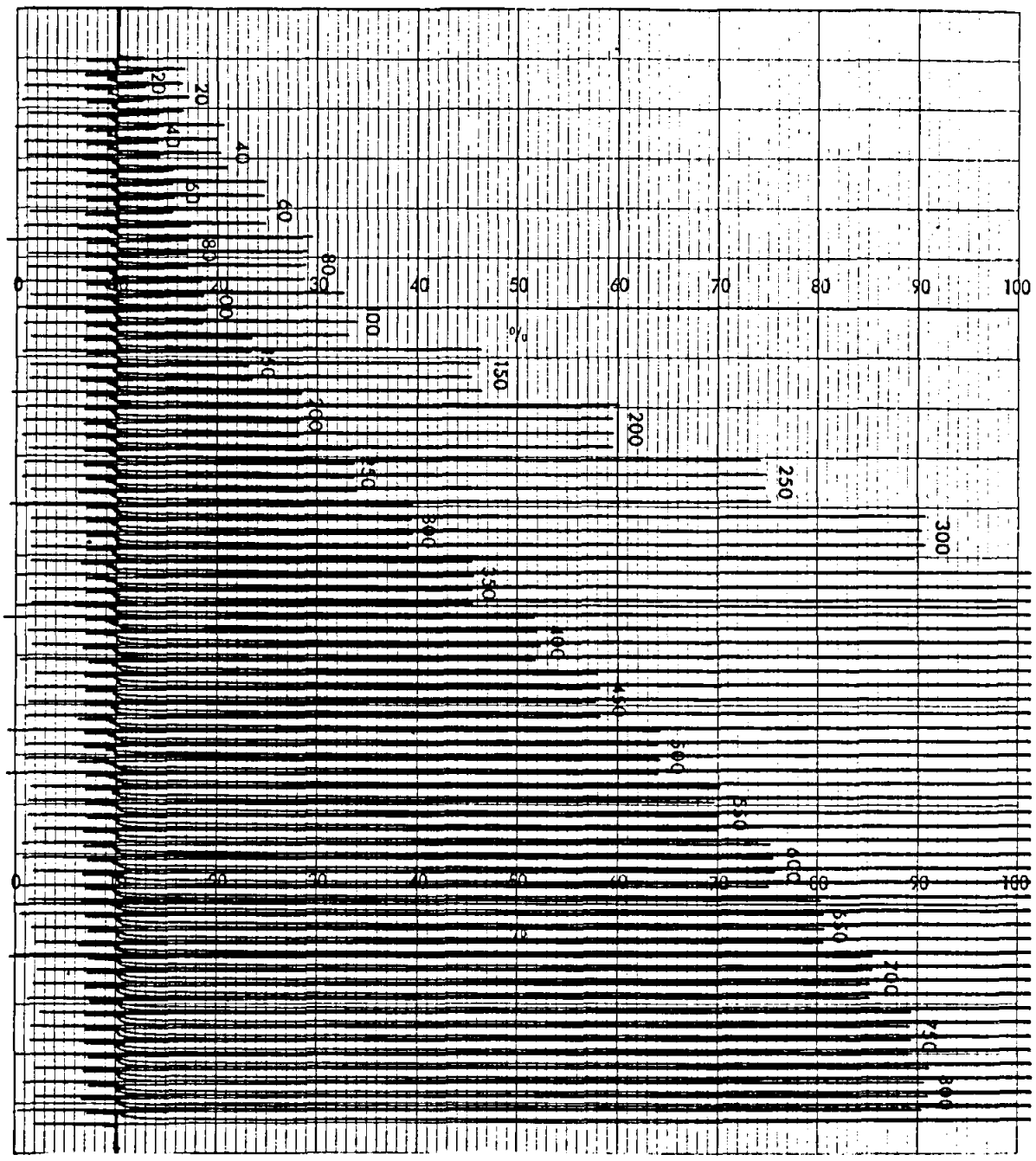
Figuur 8. Invloed van monstervolume en verdunning op lineariteit. Monstervolume = 32 µℓ. Draerstroomvloeitempo = 3,90 $cm^3 \cdot min^{-1}$. Bufferstroomvloeitempo = 0,80 $cm^3 \cdot min^{-1}$. Lynlengte = 250 cm. Buisdeursnee = 0,51 mm.



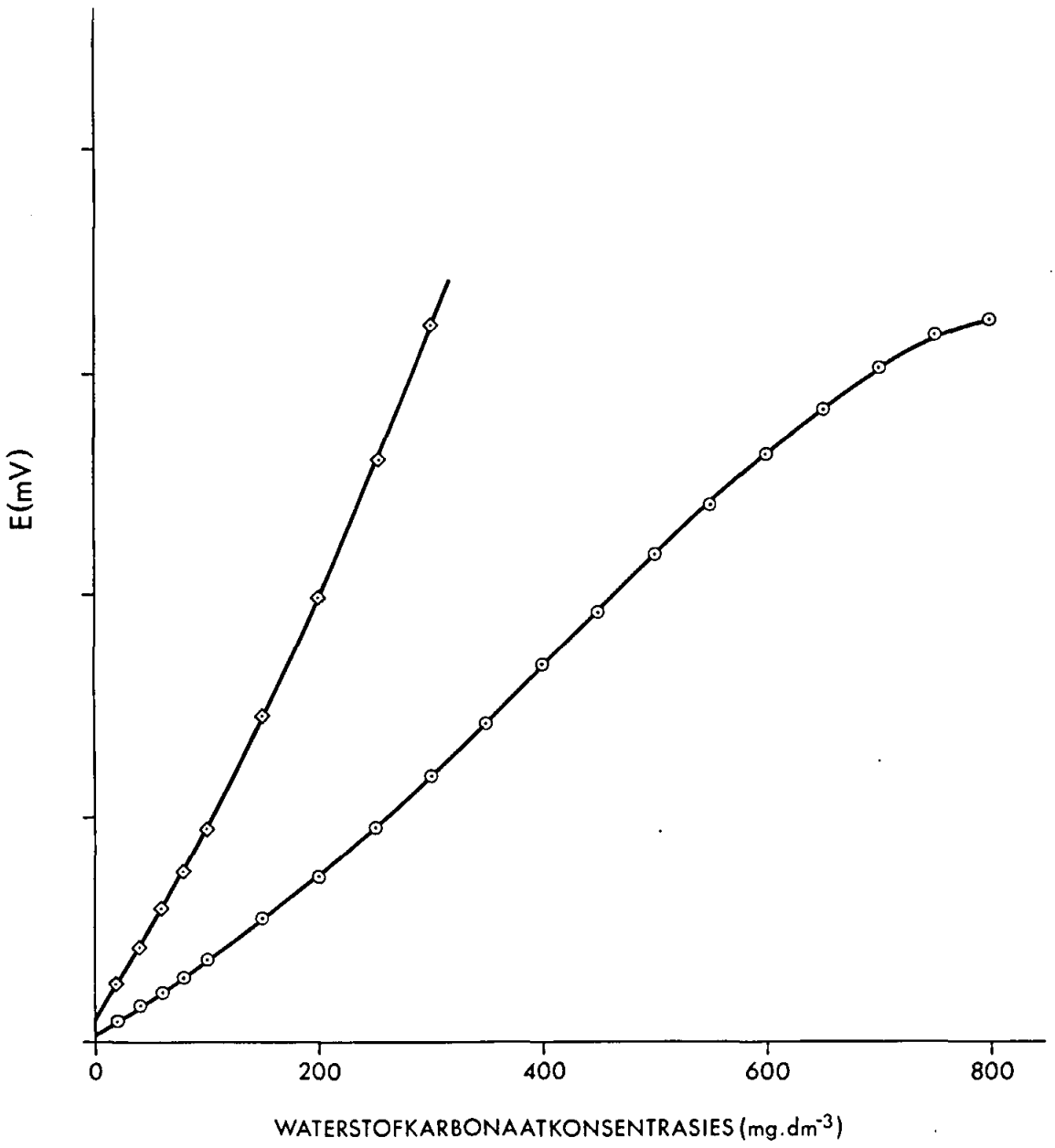
Figuur 9. Invloed van monstervolume en verdunning op lineariteit. Monstervolume = 46 µℓ. Draerstroomvloeitempo = 3,90 $cm^3 \cdot min^{-1}$. Bufferstroomvloeitempo = 0,80 $cm^3 \cdot min^{-1}$. Lynlengte = 250 cm. Buisdeursnee = 0,51 mm.



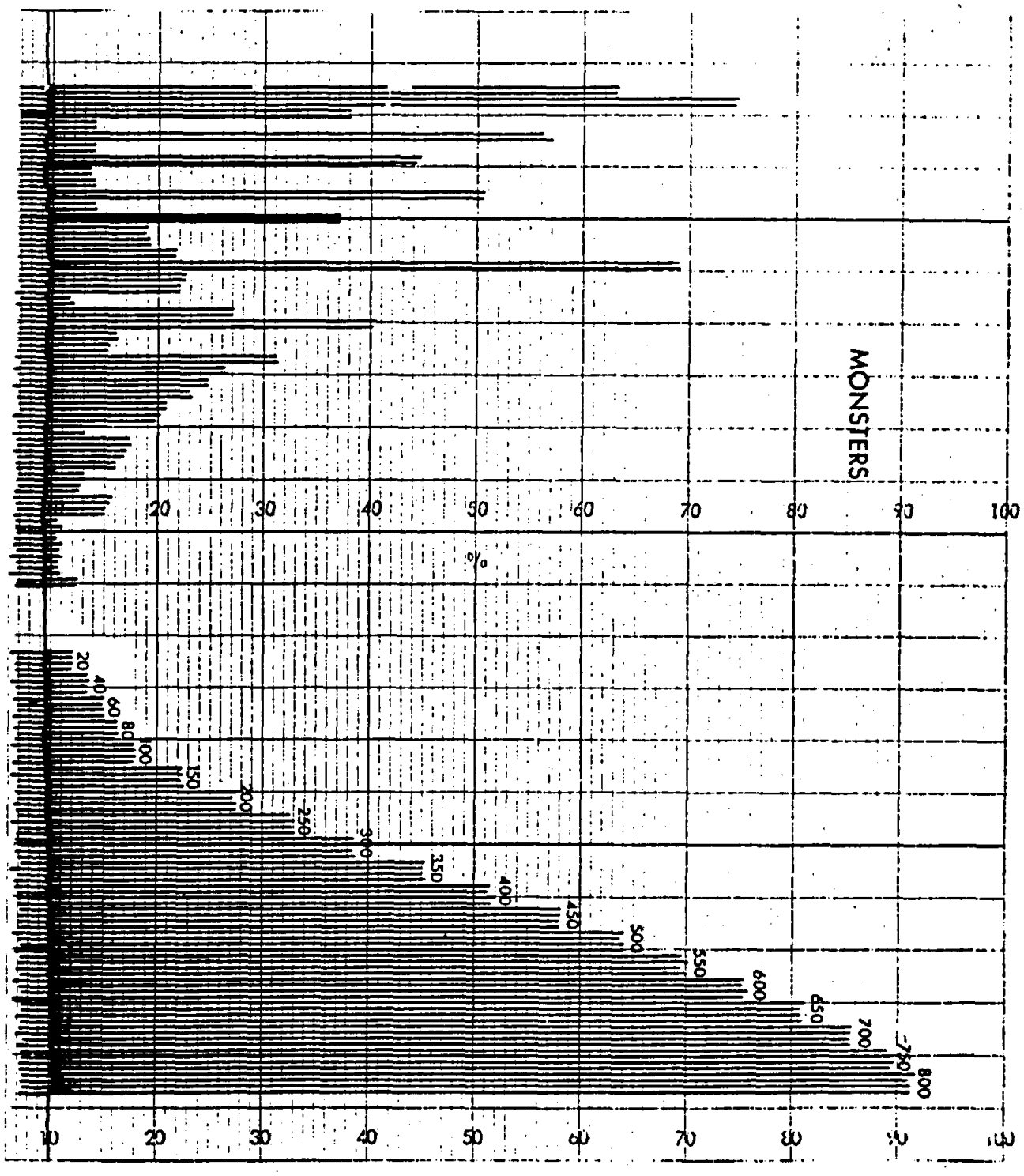
Figuur 10. Invloed van monstervolume en verdunning op lineariteit. Monstervolume = 70 µℓ. Draerstroomvloeitempo = 3,90 $cm^3 \cdot min^{-1}$. Bufferstroomvloeitempo = 0,80 $cm^3 \cdot min^{-1}$. Lynlengte = 250 cm. Buisdeursnee = 0,51 mm.



Figuur 11. Tipiese registreerder strookkaartuitdruk vir 'n reeks totale alkaliniteit standaardoplossings. Uittreësein van pH-meter verdeel om sowel lae as hoë waardes te registreer. Die getalle op die pieke dui die totale alkaliniteit as mg. per dm^3 waterstofkarbonaat aan.



Figuur 12. Kalibrasiekromme.



guur 13. Invloed van monsteroordrag en basislyndryf. Tipiese registreerder= uitdruk vir 'n verteenwoordigende lopie van 'n aantal standaarde en monsters. Die getalle op die pieke dui die totale alkaliniteit as $mg \cdot dm^{-3}$ waterstofkarbonaat aan.

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Fresenius Zeitschrift für

Automated Turbidimetric Determination of Sulphate in Surface, Ground and Domestic Water by Flow-Injection Analysis

Jacobus F. van Staden

Dept. of Chemistry, Univ. of Pretoria, Pretoria 0002, South Africa

Automatisierte turbidimetrische Bestimmung von Sulfat in Oberflächen-, Grund- und Leitungswasser mit Hilfe der Fließ-Injektions-Analyse

Zusammenfassung. Eine automatisierte einfache Modifikation der turbidimetrischen Sulfatbestimmung in Oberflächen-, Grund- und Leitungswasser mit Hilfe der Fließ-Injektion wird beschrieben. Dabei wird die eine Schleife eines Zweierventils zur Entnahme einer alkalischen EDTA-Pufferlösung, die andere Schleife damit abwechselnd für die Wasserproben verwendet. Dadurch wird ein Niederschlag, der sich an den Wänden der Durchflußzelle ansetzt, aufgelöst und somit das System sauber gehalten. Das Verfahren eignet sich zur Sulfatanalyse mit einer Geschwindigkeit von 60 Proben je Stunde bei einem Variationskoeffizient von $< 0{,}95\,\%$.

Summary. A simple, modified, automated method for the turbidimetric determination of sulphate in surface, ground and domestic water, based on the principles of the flow-injection technique, is described. The one loop of a two-position sampling valve is used to sample an alkaline buffer-EDTA solution, alternated with water samples on the other loop. This ensures that the residual precipitate, coating the walls of the flowcell, is redissolved and the system kept clean. The method is suitable for the analysis of sulphate at a rate of up to 60 samples per hour with a coefficient of variation of better than 0.95 %.

Key words: Best. von Sulfat in Wasser; Turbidimetrie; Fließ-Injektion

Introduction

Flow-injection analysis (FIA), introduced in 1975 by Růžička and Hansen [5], is a simple and convenient concept of continuous flow analysis. The advantages of this technique have been discussed in comprehensive reviews presented by Růžička and Hansen [6, 7] and Betteridge [3].

Krug et al. [4] van Staden et al. [2, 8] described methods for the determination of sulphate by measuring the turbidity of a barium sulphate suspension colorimetrically using the concept of flow-injection analysis. One of the problems associated with this method, is the build-up of barium sulphate precipitate in the flow system which tends to settle in the flowcell. This leads to low precision and ultimately blocks the manifold. The addition of an alkaline buffer-EDTA solution to redissolve the accumulated barium sulphate precipitate is one way of overcoming this problem.

Recently Betteridge et al. [1] described a method for the determination of sulphate by using a carrier solution of barium(II) ions with an excess of EDTA at pH 10, whereas the sample is acidic. The aim in water laboratories are to use undiluted water samples where possible. Due to this it is not always possible to acidify samples before analysis.

This paper reports a flow-injection procedure in which one sampling loop of a two-position sampling valve is used to sample an alkaline buffer-EDTA solution, alternated with water samples sampled on the other loop obviating acidification of water samples and reducing baseline drift.

Experimental

Apparatus

(i) Sampling Valve. A Carle microvolume two-position sampling valve (Carle Cat. No. 2014) with two sampling loops was used. Water samples were constantly sampled by the one 60 µl loop, which were alternated by using the other 100 µl loop constantly to sample an alkaline buffer-EDTA solution.

The carrier stream was supplied by a peristaltic pump and the valve system was synchronised with the sampler unit.

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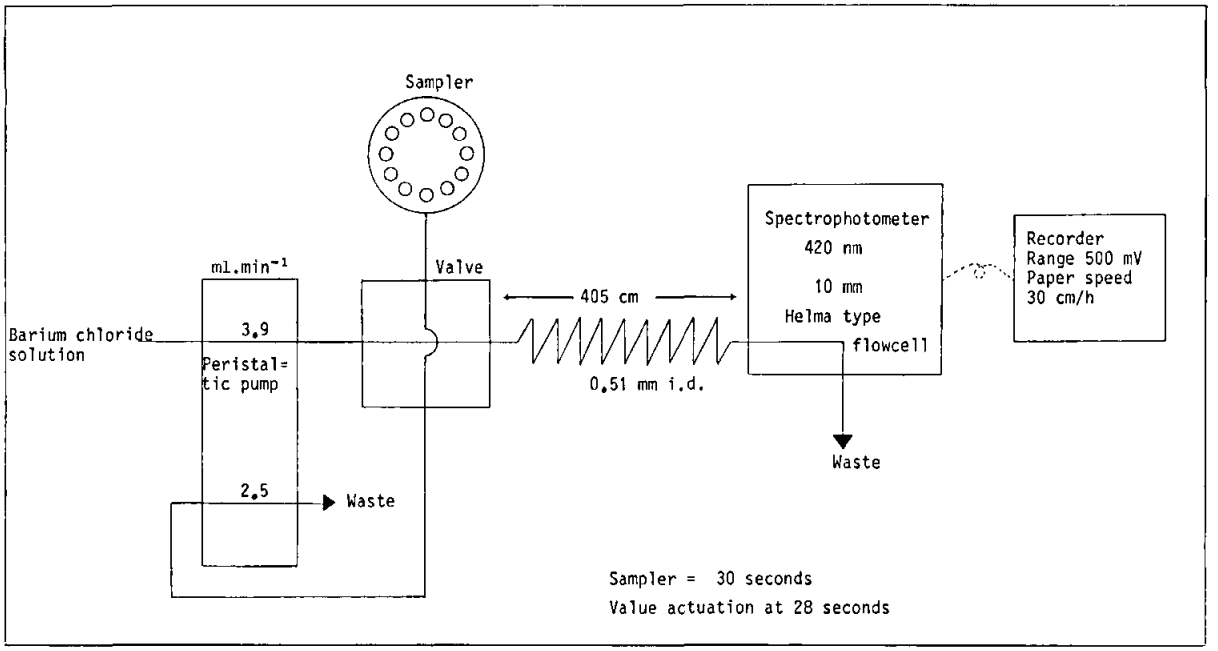

Fig. 1. Manifold and flow diagram. Tube inside diameter = 0.51 mm. Tube length given in cm as indicated. Valve loops size 60 µl for water samples and 100 µl for buffer-EDTA solution

(ii) Cenco sampler.

(iii) Cenco peristaltic pump operating at 10 rev. per minute.

(iv) Manifold (see Fig. 1).

(v) Spectrophotometer. Bausch and Lomb Spectronic 21 DV spectrophotometer (Rochester, New York) equipped with a 10 mm Helma type flow-through cell (volume 80 µl) and the sensitivity switch selected to high sensitivity.

(vi) Recorder. Mettler Model GA 12 with a recorder range of 500 mV and recorder paper speed of 30 cm/h.

Reagents

All reagents are prepared from analytical reagent quality grade unless otherwise specified.

(i) Barium Chloride Solution. Dissolve 0.20 g of thymol crystals with stirring in 500 ml of 0.005 mol · l^{-1} hydrochloric acid solution at a temperature of about 80°C. Cool to 40°C and add 1,500 ml of 0.005 mol · l^{-1} hydrochloric acid solution. Add 4 g of gelatin very slowly and swirl until dissolved. When dissolved, add 20 g of barium chloride dihydrate and dissolve. Filter, if necessary.

(ii) Buffer Solution. Dissolve 40 g of EDTA (disodium salt), 7 g of ammonium chloride and 57 ml of concentrated ammonia solution (sp. gr. 0,88) in 500 ml of distilled water. Dilute to 1 l with distilled water.

(iii) Standard Sulphate Solution. A stock solution containing 1,000 mg · l^{-1} of sulphate is prepared by dissolving 1.4787 g of anhydrous sodium sulphate, dried at 120°C for 2 h, in distilled water and diluting to 1 l. Working standard solutions in the range of 50–200 mg · l^{-1} are prepared by suitable dilution of the stock solution.

Procedure

A schematic flow diagram for the determination of sulphate is shown in Fig. 1. The manifold consists of Tygon tubing with an inside diameter of 0.51 mm cut into the required lengths and wound around suitable glass tubes with an outside diameter of 15 mm.

A barium chloride reagent carrier stream was provided at a constant flow rate of 3.9 ml · min^{-1} by means of a peristaltic pump. Samples from an automated sampler were injected automatically from a 60 µl sampling loop into the reagent stream by means of a Carle micro-volume two-position sampling valve. This was alternated by injecting automatically 100 µl of alkaline buffer-EDTA solution into the reagent stream from the other sampling loop. The above mentioned process is achieved by placing the water samples in every second cup of the automated sampler, alternating the samples by placing alkaline buffer-EDTA solution in the cups between samples. A 30 s sampling cycle is used between sampling a water sample and sampling buffer-EDTA solution giving the system a total sampling capacity of 120 per hour. This means a sampling capacity of 60 water samples per hour. The valve system is actuated on a time basis which is correlated with the sampler unit. The sampling valve actuates every 28 s after movement of the sampler to the next sample.

Results and Discussion

A typical representative strip-chart recorder output at a sampling rate of 60 actual water samples per hour is illustrated in Fig. 2. The negative peaks between samples are due to the alternative sampling of alkaline buffer-EDTA solution. The analysis were performed in a random order, to test carry-over effects. Carry-over from one sample to another is neglible. No baseline drift was experienced.

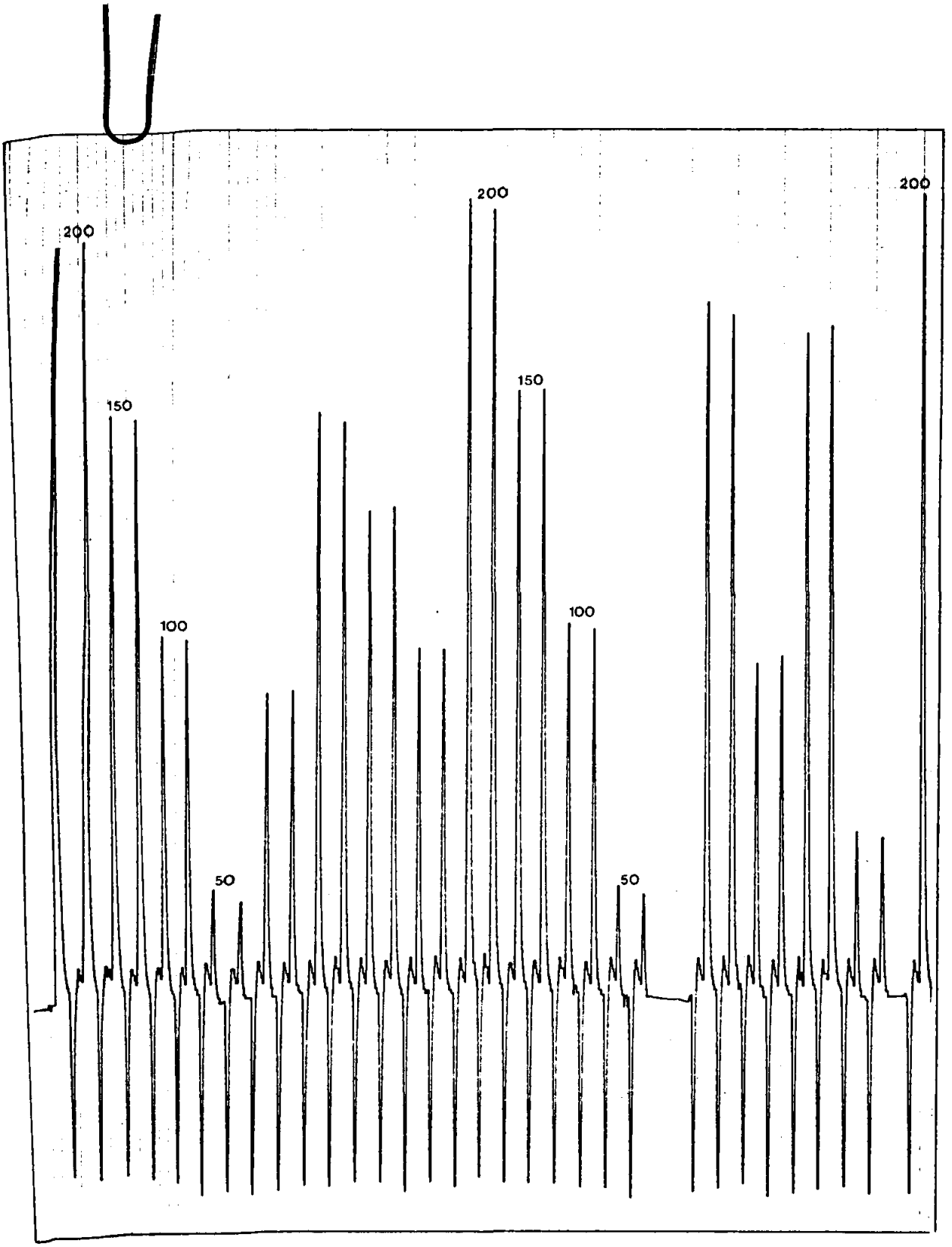

Fig. 2. Recorder tracing for the flow-injection determination of sulphate in water. Recorder paper speed 30 cm/h. Recorder range 500 mV. Sulphate concentrations in $mg \cdot l^{-1}$. Negative peaks due to alkaline buffer-EDTA solution sampled

Table 1. Reproducibility test on a series of standard sulphate solutions

Theoretical mg sulphate/ l^{-1}	Number of tests	Coefficient of variation %
50	10	0.95
75	10	0.87
100	10	0.90
125	10	0.66
150	10	0.46
175	10	0.42
200	10	0.69

Table 2. Performance of the proposed FIA-method for sulphate

Sample	Number of tests	Automated segmented method. Sulphate concentration in $mg \cdot l^{-1}$	FIA-method. Sulphate concentration in $mg \cdot l^{-1}$	Coefficient of variation
1	10	92	95	0.81
2	10	149	154	0.71
3	10	137	135	0.91
4	10	103	104	0.43
5	10	184	179	0.61
6	10	105	101	0.49
7	10	173	174	0.51
8	10	59	63	0.93
9	10	196	187	0.46
10	10	54	49	0.84
11	10	564[a]	551[a]	0.79
12	10	1,351[a]	1,377[a]	0.57

[a] Water samples diluted to be in analyzing range

The reproducibility of the proposed method was tested on standard sulphate solutions (Table 1) and water samples (Table 2). The coefficient of variation for standard sulphate solutions and for water samples having different concentrations of sulphate, is less than 0.95% on 10 tests of each sample.

The proposed FIA-method compares favourably with the standard automated segmented method as seen from Table 2.

Conclusion. The flow-injection procedure described here is suitable for carrying out sulphate analysis at a rate of approximately 60 water samples per hour. Baseline drift can be eliminated by alternatively sampling an alkaline buffer-EDTA solution.

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Automated Prevalve Sample Filtration in Flow Injection Analysis: Determination of Sulphate in Water Removing Suspended Solids and Colour Before Sampling*

Jacobus F. van Staden

Department of Chemistry, University of Pretoria, 0002 Pretoria, South Africa

Automatische Filtration vor dem Probeneinlaßventil in der Fließ-Injektionsanalyse: Entfernung von Festsubstanzen und Farbstoffen bei der Sulfatbestimmung in Wasser

Zusammenfassung. Suspendierte Feststoffe, organische Substanzen und Farbstoffe stellen die Hauptstörquellen bei der turbidimetrisch-spektralphotometrischen Sulfatbestimmung bei 420 nm dar. Bei dem vorgeschlagenen Fließ-Injektionsverfahren werden diese Störungen automatisch mit Hilfe eines Aktivkohlefilters entfernt, das zwischen Probengeber und Probenventil angeordnet ist. Mit dem vorgeschlagenen System werden die gleichen Ergebnisse erhalten wie mit einer Standardmethode sowie einem Segmentierungsverfahren mit manueller Entfernung der Störungen vor der Probeneingabe. Die neue Methode eignet sich für die Sulfatbestimmung in Oberflächen-, Grund- und Haushaltswasser bis zu 200 mg/l bei einer Geschwindigkeit von 60 Proben je Stunde. Der Variationskoeffizient ist besser als 1 %.

Summary. Suspended solids and the presence of organic substances and colour are the main interferences in the turbidimetric spectrophotometric determination of sulphate at 420 nm in water. An automated flow-injection procedure is proposed in which these interferences are automatically removed by using an active carbon filter, which is incorporated in the flow system between the sampler and the sampling valve system. With this automated prevalve sample filter the proposed turbidimetric method gives the same results as a standard flow injection and an automated segmented method where the above mentioned interferences are manually removed prior to sampling. The method is applicable for the analysis of sulphate in surface, ground and domestic waters in the concentration range up to 200 mg/l at a sampling rate of up to 60 samples per hour with a coefficient of variation of better than 1 %.

Introduction

A substantial number of water samples are analysed each year world-wide to determine various constituents, including sulphate. The normal range for sulphate in surface, ground and domestic waters is in the concentration range of up to 200 mg/l. The limited number of samples above this concentration range are manually diluted before analysis. For the routine analysis of sulphate, the automated flow injection turbidimetric determination, previously described [1], should be very attractive, providing a concentration range of up to 200 mg/l and a sampling rate of up to 60 samples per hour.

In the turbidimetric determination of sulphate, the sulphate ions are converted to an insoluble barium sulphate suspension in a gelatin-thymol medium. The degree of suspension is controlled by several factors and therefore the concentrations related to reagents and precautions preparing the reagents must be strictly followed. Hydrochloric acid is added to the barium chloride carrier solution to prevent the formation of a precipitate of barium sulphite which may interfere. Furthermore, the hydrochloric acid prevents the precipitation of carbonate, chromate, phosphate and oxalate of barium.

The build-up of barium sulphate precipitate in the flow system is one of the problems associated with this method. This leads to low precision and ultimately blocks the manifold. This is avoided [1] by using a procedure in which one of the sampling loops of a two-position sampling valve is used to sample an alkaline buffer-EDTA solution, alternated with water samples sampled from the other loop.

Suspended solids and the presence of organic substances are a real problem which interferes in the turbidimetric determination of sulphate at 420 nm in surface, ground and domestic waters. Furthermore, suspended solids tend to settle in the flow system and valve loops which leads to changing characteristics associated with the flow system. This causes low precision and sometimes blocks the manifold system entirely.

Slanina et al. [2] describe a method using active carbon as a selective filter for organic substances in their fast determination of nitrate in rain and surface waters by means of UV spectrophotometry. In this method the active carbon filter forms part of the manifold system. This idea was tested in the flow injection determination of sulphate, but was not successful due to the following problems: suspended solids still tend to settle in the valve loops and sometimes block the manifold system, and the whole flow injection analysis system is disrupted, when the active carbon filter has to be replaced.

It was obvious that the best way to solve this problem was the incorporation of the active carbon filter as an automated prevalve filter in the flow injection system. This paper therefore reports the application of an active prevalve carbon

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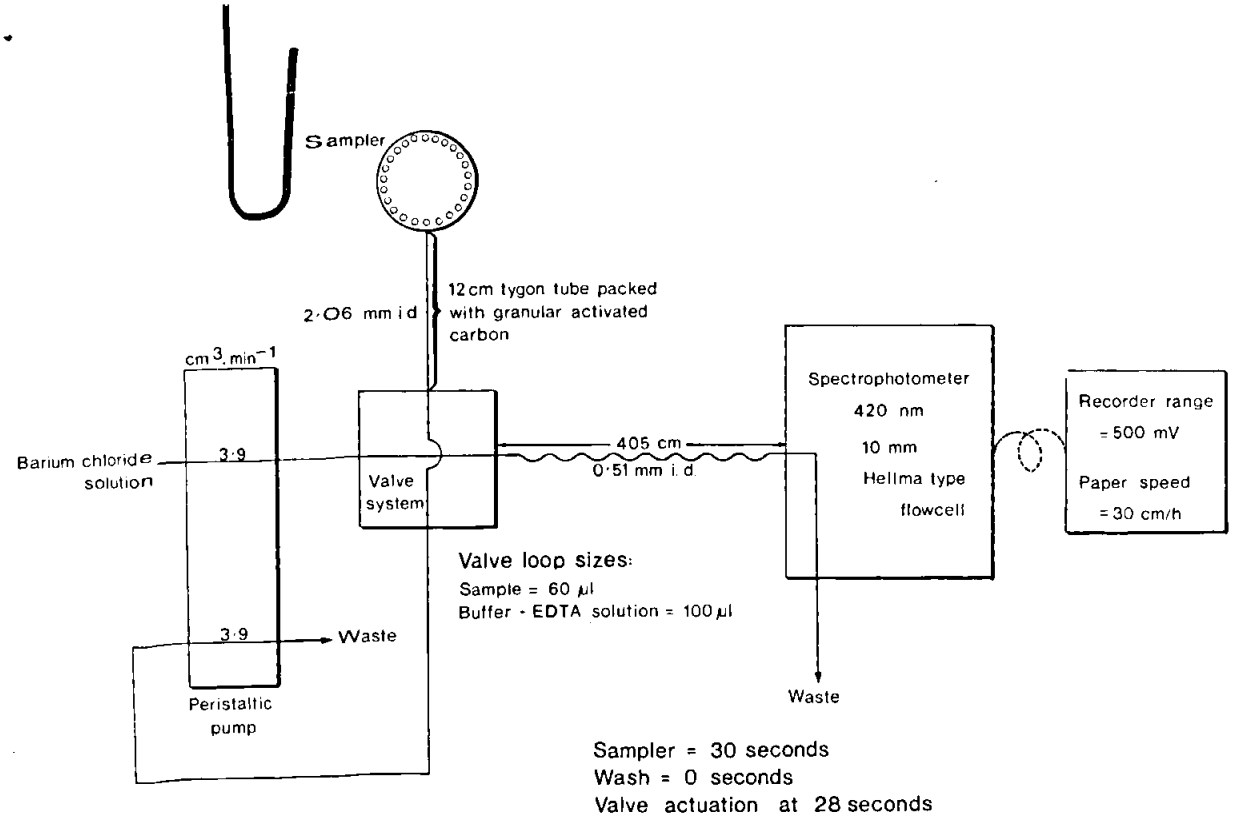

Fig. 1. Schematic flow diagram for the determination of sulphate in surface, ground and domestic waters using automated prevalve sample treatment to remove suspended solids and colour before sampling. Valve loop sizes: 60 µl water samples injected by one loop alternated with 100 µl buffer-EDTA solution from the other loop. Sampling rate: 60 water samples per h. Tube length and i.d. are given in cm and mm, respectively

filter for the turbidimetric determination of sulphate in surface, ground and domestic waters.

Experimental

Apparatus

(i) Active Carbon Filter. A 12 cm Tygon tube with an inside diameter of 2.06 mm packed with granular activated carbon is used as a filter system. This system is incorporated as part of the flow diagram between the sampler and the sampling valve system as illustrated in Fig. 1.

(ii) Sampling Valve. A Carle microvolume two-position sampling valve (Carle Cat. No. 2014) with two sampling loops was used. Water samples were constantly sampled by one 60 µl loop, which were alternated by using the other 100 µl loop constantly to sample an alkaline buffer-EDTA solution. The carrier stream was supplied with a peristaltic pump and the sampling valve system was synchronised with the sampler unit.

(iii) Cenco sampler.

(iv) Cenco peristaltic pump operating at 10 rev. per minute.

(v) Manifold (see Fig. 1).

(vi) Spectrophotometer. Bausch and Lomb Spectronic 21DV spectrophotometer (Rochester, New York) equipped with a 10 mm Hellma type flow-through cell (volume 80 µl). The sensitivity setting selected was the highest possible.

Reagents

All reagents were prepared from analytical reagent quality grade unless otherwise specified.

Table 1. Reproducibility test on a series of standard sulphate solutions

Theoretical mg/l sulphate	Number of tests	Coefficient of variation %
50	12	0.99
75	12	0.91
100	12	0.88
125	12	0.71
150	12	0.44
175	12	0.41
200	12	0.62

(i) Barium Chloride Solution. Dissolve 0.20 g of thymol crystals with stirring in 500 ml of 0.005 mol/l hydrochloric acid solution at a temperature of about 80°C. Cool to 40°C and add 500 ml of 0.005 mol/l hydrochloric acid solution. Add 4 g of gelatin very slowly and swirl until dissolved. When dissolved, add 20 g of barium chloride dihydrate and dissolve. Filter, if necessary.

(ii) Buffer Solution. Dissolve 40 g of EDTA (disodium salt), 7 g of ammonium chloride and 57 ml of concentrated ammonia solution (sp. gr. 0.88) in 500 ml of distilled water. Dilute to 1 l with distilled water.

(iii) Standard Sulphate Solution. Prepare a stock solution containing 1,000 mg/l of sulphate by dissolving 1.4787 g of anhydrous sodium sulphate, dried at 120°C for 2 h, in distilled water and diluting to 1 l. Prepare working standard solutions in the range of 50–200 mg/l by suitable dilution of the stock solution.

Table 2. Reproducibility test on a series of water samples

Sample	Number of tests	Sulphate concentration in mg/l	Coefficient of variation %
1	12	179	0.59
2	12	51	0.91
3	12	143	0.43
4	12	77	0.71
5	12	61	0.87
6	12	191	0.57
7	12	113	0.53
8	12	57	0.96
9	12	181	0.63
10	12	101	0.51

Table 3. Accuracy test of the proposed FIA-method against standard procedures

Sample	Proposed FIA-method. Sulphate concentration in mg/l	Automated segmented method. Sulphate concentration in mg/l	FIA-method previously described [1]. Sulphate concentration in mg/l
1	179	182	180
2	51	53	52
3	143	141	143
4	77	75	78
5	61	66	63
6	191	193	192
7	113	113	114
8	57	59	56
9	181	179	181
10	101	99	102

Table 4. Results of sulphate content in water samples with and without a carbon filter in the FIA-method

Sample number	Sulphate content in mg/l	
	With filter	Without filter
1	179	184
2	51	63
3	143	148
4	77	81
5	61	69
6	191	197
7	113	124
8	57	70
9	181	187
10	101	109

Procedure

A schematic flow diagram for the flow injection system is outlined in Fig. 1. The manifold consists of Tygon tubing with an inside diameter of 0.51 mm cut into the required lengths and wound around suitable glass tubes with an outside diameter of 15 mm.

A barium chloride reagent carrier stream is provided at a constant flow rate of 3.9 ml min^{-1} by means of a peristaltic pump. Samples taken from the turntable of an automatic sampler are pumped through a 12 cm 2.06 mm i.d. tube packed with granular activated carbon into a sample loop by means of a peristaltic pump. In this way suspended solids and colour are automatically removed before sampling. Filtered samples are injected automatically from a 60 µl sampling loop into the reagent stream by means of a Carle microvolume two-position sampling valve. This is alternated by injecting automatically 100 µl of alkaline buffer-EDTA solution into the reagent stream from the other sampling loop. The above mentioned process is achieved by placing the water samples in every second cup of the automated sampler, and alkaline buffer-EDTA solution in the cups between samples. A 30 s sampling cycle is used between sampling a water sample and sampling buffer-EDTA solution giving the system a total sampling capacity of 120 per hour. This means a sampling capacity of 60 water samples per hour. The valve system is actuated on a time basis which is correlated with the sampler unit. The sampling valve actuates every 28 s after movement of the sampler to the next sample.

Results and Discussion

Buffer-EDTA solution from the cups between samples are also pumped through the active carbon filter and these compounds might also be adsorbed by the active carbon, thus reducing the lifetime of the filter drastically. This has been investigated and no dramatic reduction in lifetime was observed. Another possibility is that the active carbon could adsorb sulphate ions. Standard sulphate solutions as well manually filtered samples were analysed with and without the active carbon filter and no difference in absorbance was recorded at 420 nm. The filter must be replaced after about 400–500 determinations and this is done on-line between samples without disturbing the manifold system.

Analysis of samples was performed in a random order to test carry-over effects. Carry-over from one sample to another was neglible. No baseline drift was experienced.

The reproducibility of the proposed method was tested on standard sulphate solutions (Table 1) and water samples (Table 2). The coefficient of variation for standard sulphate solutions and for water samples having different concentrations of sulphate, was less than 1% on 12 tests of each sample.

The accuracy of the proposed flow injection analysis (FIA) method was tested by comparing the results of 10 water samples, taken from surface, ground and domestic systems, with those obtained by the previously described FIA method [1] and a standard automated segmented method where samples were manually filtered before analysis. Results compare favourably as can be seen from Table 3. Samples were also analysed with and without the carbon filter to get an indication of the interference by organic substances and colour and to prove the success of the proposed FIA method (Table 4).

Acknowledgements. The author expresses his gratitude to the Council for Scientific and Industrial Research, Pretoria and to the University of Pretoria for financial support and also to the Hydrological Research Institute, Pretoria, for supplying the analysed samples. The author thanks Mrs. K. J. Schneider for assistance in preparing the manuscript.

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BYLAAG 5

VLOEI-INSPUIT TURBIDIMETRIESE ANALISE VAN SULFAAT. DEEL 1. OUTOMATIESE VOORKLEPFILTRASIE MET GEAKTIVEERDE KOOLSTOFFILTREERPAPIER.

J.F.VAN STADEN
Departement Chemie
Universiteit van Pretoria
PRETORIA 0002

SUMMARY

Suspended solids and the presence of organic substances and colour are the main interferences in the turbidimetric spectrophotometric determination of sulphate at 420 nm in water. This problem has been solved by the develop= ment of an automated prevalve filter system consisting of a 12 cm Tygon tube with i.d. of 2,06 mm packed with activated carbon. The abovementioned automated prevalve filter system has now been improved by developing a system where activated carbon filter paper is used. It is much more easier to replace the latter in routine laboratories. The method is applicable for the analysis of sulphate at a sampling rate of up to 60 samples per hour with a coefficient of variation of better than 1%.

INLEIDING

Sulfaat, wat oor die algemeen wyd verspreid in die natuur voorkom, is teenwoordig in natuurlike water in konsentrasies wat strek vanaf nul tot 'n hele aantal duisend milligram per dm^3. Dit word ook aangetref in industriële afval as gevolg van die vrystelling vanaf aanlegte soos looierye, pulpmeules, tekstielmeules en ander aanlegte waarin swaelsuur gebruik word. Hierdie industriële afval beland uiteindelik in riviere en damme waar die sulfaat dan besoedeling veroorsaak. Weens die purgerende fisiologiese effek op die menslike liggaam, het die Verenigde State se "Public Health Service Drinking Water Standards" van 1946 voorgestel dat die sulfaatinhoud nie die limiet van 250 $mg \cdot dm^{-3}$ in aanvaarbare watervoorsienings= netwerke sal oorskry nie. Die toenemende neiging vir die eliminasie van besoedeling in water het gelei tot die aanvraag na 'n metode vir die bepa= ling van sulfaat in water waarin die analisefrekwens verhoog kan word.

Die mikro-balans en ander gesofistikeerde tegnieke wat gebruik word om klein hoeveelhede materiaal te hanteer, maak die gravimetriese prosedure (presipitasie as bariumsulfaat) steeds bruikbaar, maar heeltemal onprakties om groot hoeveelhede monsters in 'n beperkte tyd te hanteer. Gevolglik is verskeie spektrofotometriese metodes ontwikkel vir die bepaling van sulfaat.

Die drie metodes wat oor die algemeen universeel die meeste gebruik word, is die bariumchloroanilaatmetode (Bertolacini en Barney, 1957; Agterden= bos en Martinius, 1964), die metieltimolbloumetode (Lazrus, Hill en Lodge, 1965) en die bariumsulfaat turbidimetriese prosedure (Sheen et al, 1935). In die geval van die chloro-anilaat- en metieltimolblouprosedures word bariumsulfaat as een van die produkte gevorm, terwyl 'n ekwivalente hoeveel= heid van die gekleurde anioonvorm van die reagens vrygestel word, wat dan

kolorimetries bepaal word. Hierdie metodes is egter nie steuringsvry nie en veral die swaar metaalkatione moet verwyder word met behulp van ioonuit= ruilingstegnieke. So steur baie katione soos Ca^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Fe^{3+} en Al^{3+} deurdat hulle minoplosbare chloro-anilate vorm. In hierdie geval word die verwydering van bogenoemde katione deur 'n sterk katioonuitruilhars in die waterstofvorm aanbeveel. Dit is prakties uitvoerbaar by sekere geselek= teerde watermonsters soos kraanwater waar steurings nie in oorvloed teen= woordig is nie. Dit skep egter oor die algemeen probleme by die grootste gedeelte van die algemene omgewingswaters waar steuringselemente wel voor= kom weens besoedeling.

Ten spyte van die onsekerhede kenmerkend van turbidimetriese prosedures, is bariumsulfaat suspensies goed bestudeer en vind die metode bruikbare toepassing in die bepaling van sulfaat. Die metode word aanbeveel as 'n standaard metode vir die toets vir die sulfaatioon in water en afvalwater (American Society for testing and materials, 1975).

In die turbidimetriese bepaling van sulfaat, word die sulfaatione omge= skakel na 'n minoplosbare bariumsulfaatsuspensie in 'n gelatien-timol medium deur die byvoeging van 'n oormaat bariumchloried reagens.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightleftarrows BaSO_4\downarrow$$

Die akkuraatheid en presisie van die turbidimetriese bepaling van sulfaat hang van die kristalvorm en die verspreiding van die verskillende groottes van die ligverstrooiende deeltjies in die suspensie af. Die graad van ver= strooiing word deur verskeie faktore beheer en is baie afhanklik van reak= sietoestande. Dit is dus noodsaaklik dat die vereistes ten opsigte van konsentrasies en die voorsorgmaatreëls ten opsigte van die voorbereiding van die reagense streng gevolg word. In vloei-inspuitanalise is dit egter moontlik om elke standaard en monster op presies dieselfde wyse te hanteer

sodat reaksietoestande in so 'n sisteem konstant bly. Die byvoeging van soutsuur by die bariumchloriedoplossing verhoed die presipitasie van sulfiet, karbonaat, chromaat, fosfaat en oksalaat met barium.

Een van die probleme wat geassosieer is met hierdie metode is die opbou van bariumsulfaat presipitaat wat veral in die vloeisel en op die wande van die buise in die vloeisisteem akkumuleer. Dit veroorsaak 'n lae presisie en blokkeer uiteindelik die vermengingsisteem. Dit word vermy (Van Staden, 1982) deur 'n prosedure te gebruik waarin een van die monsternemingslusse van 'n tweeposisie monsternemingsklep gebruik word om 'n alkaliese buffer-EDTA oplossing te monster. Dit word afgewissel met watermonsters gemonster deur die tweede lus. Sodoende word basislyndryf uitgeskakel.

Gesuspendeerde materiaal en die teenwoordigheid van organiese stowwe (kleur) skep egter nog steeds probleme. Dit steur in die turbidimetriese bepaling van sulfaat. Gesuspendeerde vaste deeltjies is verder geneig om in die vloei= sisteem en kleplusse te akkumuleer. Dit veroorsaak 'n verandering in die vloeidinamika van die sisteem, wat weer tot lae presisie lei. Soms word die vloeisisteem heeltemal geblokkeer.

Van Staden (1982) het 'n metode beskryf waardeur gesuspendeerde materiaal en kleur met behulp van outomatiese voorklepfiltrasie verwyder is. In die metode is gebruik gemaak van 'n 12 cm tygonbuis met 'n binne-deursnee van 2,06 mm wat met korrelrige geaktiveerde koolstof gepak is. Die metode het goed ge= funksioneer, maar daar is gevind dat vervanging van die tygonbuis probleme kan lewer in roetinelaboratoriums. Die pakking van die buis is tydrowend. Dit is nie altyd moontlik om twee buise te pak wat identies is nie. Die buis kan ook te dig gepak word sodat vloeiprobleme ontstaan.

Gevolglik is hierdie outomatiese voorklepfiltreersisteem nou verder verfyn deur 'n sisteem te ontwikkel waar geaktiveerde koolstoffiltreerpapier ge= bruik word.

EKSPERIMENTEEL

Apparaat

Geaktiveerde koolstoffiltreerder

Die geaktiveerde koolstoffiltreersisteem word skematies in Figuur 1 voorge= stel. Die sisteem word met een of meer skywe geaktiveerde filtreerpapier (Carl Schleicher and Schüll, Postfach 4, D-3354, West-Germany; Active Carbon Paper No. 508) gepak. Die sisteem bestaan uit twee dele a en b wat inmekaar geskroef word. (Kyk sy-aansig Figuur 1). Die dwarsdeursnee van die twee dele a en b met aansig van bo toon die volgende (Figuur 1): Beide gedeeltes is voorsien van siffies wat die ergste gesuspendeerde deeltjies kan keer. Vuil watermonsters vanaf die monsternemer beweeg by gedeelte b in, die siffie keer die ergste gesuspendeerde deeltjies en kleur word deur die geaktiveerde filtreerpapier verwyder. Die siffie by gedeelte a is daar geplaas om te verhoed dat van die geaktiveerde koolstofdeeltjies op die filtreerpapier na die analitiese kanaal beweeg. Die gedeelte a bevat verder ook 'n O-ring (kyk dwarsdeursnee figuur 1) om lekkasie van lug te voorkom en die sisteem dig te sluit. Hierdie gedeelte is verder effens skuins afgewerk om die sisteem beter te laat funksioneer. Die skoon monster word vanuit hierdie gedeelte aan die analitiese kanaal van die vloeisisteem voorsien. Die filtreersisteem word geïnkorporeer as deel van die vloeidiagram tussen die monsternemer en die monsternemingsklepsisteem soos geïllustreer in Figuur 2.

Dieselfde monsternemingsklep en lusse, monsternemer, peristaltiese pomp en spektrofotometer met deurvloeisel as in bylaag 6 is gebruik. By die vermengingsisteem (Figuur 2) is die enigste verskil die vervanging van die geaktiveerde koolstoftygonbuis met 'n geaktiveerde koolstoffiltreerpapier= sisteem.

Die voorbereiding van die reagense en standaarde is in bylaag 6 beskryf.

PROSEDURE

Dieselfde prosedure as in bylaag 6 is gevolg.

RESULTATE EN BESPREKING

Buffer-EDTA oplossing van die monsterhouers tussen werklike monsters word ook deur die voorklepfiltreersisteem gepomp. Hierdie verbindings kon ook deur die geaktiveerde filtreerpapier geadsorbeer word, wat sou veroorsaak dat die leeftyd van die filtreerpapier drasties ingekort word. Hierdie moontlikheid is ondersoek en daar is gevind dat dit geen invloed uitoefen nie. 'n Tweede moontlikheid is dat die geaktiveerde filtreerpapier sulfaatione kon adsorbeer. Standaard sulfaatoplossings sowel as handgefiltreerde monsters en gewone kraanwater is met en sonder die geaktiveerde voorklepfiltreersisteem ge-analiseer. Geen verskil in absorbansie is waargeneem nie. Die leeftyd van die filtreerpapier word bepaal deur die geaardheid van en aantal vaste deel= tjies wat in monsters teenwoordig is. Daar is gevind dat meer as 500 monsters deur die filtreersisteem gepomp kan word voordat die filtreerpapier vervang moet word. Dit moet geskied sodra daar enige tekens is dat die presisie ver= swak voordat dit blyk of daar 'n aanduiding van blokkasie is. Dit kan gedoen word deur die hele voorklepsisteem te vervang met 'n tweede terwyl die sis= teem in bedryf is sonder om die vermengingsisteem te versteur.

Die invloed van monsteroordrag oor die konsentrasiegebied van 50 tot 200 $mg \cdot dm^{-3}$ sulfaat is geëvalueer deur analises na willekeur uit te voer. Oordrag van een monster na 'n tweede is weglaatbaar klein. Geen basislynver= skuiwing is ondervind nie.

Die presisie van die metode is op 10 verskillende watermonsters getoets wat oor die konsentrasiegebied van 50 tot 200 $mg \cdot dm^{-3}$ versprei is. Die standaardafwyking vir die watermonsters met verskillende sulfaatkonsentrasies is minder as 1% op 17 toetse vir elke monster.

Die akkuraatheid van die voorgestelde VIA metode is getoets deur die resul= tate van 20 oppervlakte-, grond- en huishoudelike watermonsters te vergelyk met 'n vorige VIA metode (Van Staden, 1982) en 'n standaard outomatiese geseg= menteerde metode waar die monsters met die hand gefiltreer is voor analise. (Kyk tabel 1). Om te toets of die voorgestelde metode geskik is vir toe= passing in wateranalise, is die t-distribusietoets (K. Eckschlager, 1969) op die voorgestelde VIA- en standaard outomatiese gesegmenteerde metode uit= gevoer. Daar is gevind dat die eksperimentele berekende t-waarde van 0,692 kleiner is as die getabuleerde t-waarde van 2,093 op die 95% betroubaarheids= interval. Daar is dus geen statisties betekenisvolle verskil op bogenoemde betroubaarheidsinterval nie. Die verskil in resultate kan verduidelik word aan die hand van toevallige foute. Die voorgestelde metode is dus geskik vir die bepaling van sulfaat in water. Die akkuraatheid van die voorgestelde metode is ook getoets deur bekende hoeveelhede sulfaat by watermonsters te voeg en te bepaal hoeveel van die bygevoegde sulfaat herwin is (Tabel 2). Die herwinbaarheid volgens hierdie metode is gemiddeld 99,8%.

ERKENNING

Hierdie projek is uitgevoer met finansiële ondersteuning van die Waternavor= singskommissie, die Wetenskaplike en Nywerheidsnavorsingsraad en die

Universiteit van Pretoria. Die Hidrologiese Navorsingsinstituut, Pretoria word bedank vir die verskaffing van geanaliseerde watermonsters.

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Van Staden, J.F. (1982). Automated Prevalve Sample Filtration in Flow Injection Analysis. Determination of Sulphate in Water Removing suspended solids and colour before sampling. Fresenius Z. Anal. Chem. 312, 438.

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TABEL 1

Akkuraatheidstoets van die voorgestelde VIA-metode teen standaard prosedures.

Monster	Voorgestelde VIA-metode Sulfaatkonsentrasie in $mg \cdot dm^{-3}$	Outomatiese gesegmenteerde metode Sulfaatkonsentrasie in $mg \cdot dm^{-3}$	VIA-metode alreeds beskryf (Van Staden 1982). Sulfaatkonsentrasie in $mg \cdot dm^{-3}$
1	180	183	181
2	53	52	51
3	75	78	76
4	121	120	121
5	173	170	174
6	81	79	82
7	193	196	195
8	172	169	173
9	87	84	84
10	65	65	61
11	195	194	190
12	149	151	151
13	136	136	134
14	59	59	61
15	113	112	110
16	177	178	177
17	96	99	97
18	141	146	142
19	159	157	158
20	119	124	120

VIA = vloei-inspuitanalise

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TABEL 2

Herwinningstoetse met die voorgestelde VIA metode op drie watermonsters met verskillende sulfaatkonsentrasies.

Monster	Sulfaatkonsentrasie in watermonster $mg \cdot dm^{-3}$	Herwinningstoets		
		Sulfaat bygevoeg mg.	Sulfaat herwin mg.	% Herwin
1	53	5,0	4,92	98,4
		10,0	9,98	99,8
		15,0	15,02	100,1
2	195	5,0	5,01	100,2
		10,0	10,03	100,3
		15,0	15,01	100,1
3	96	5,0	4,97	99,4
		10,0	9,96	99,6
		15,0	14,99	99,9

Gemiddelde % herwinning = 99,8

VIA = vloei-inspuitanalise

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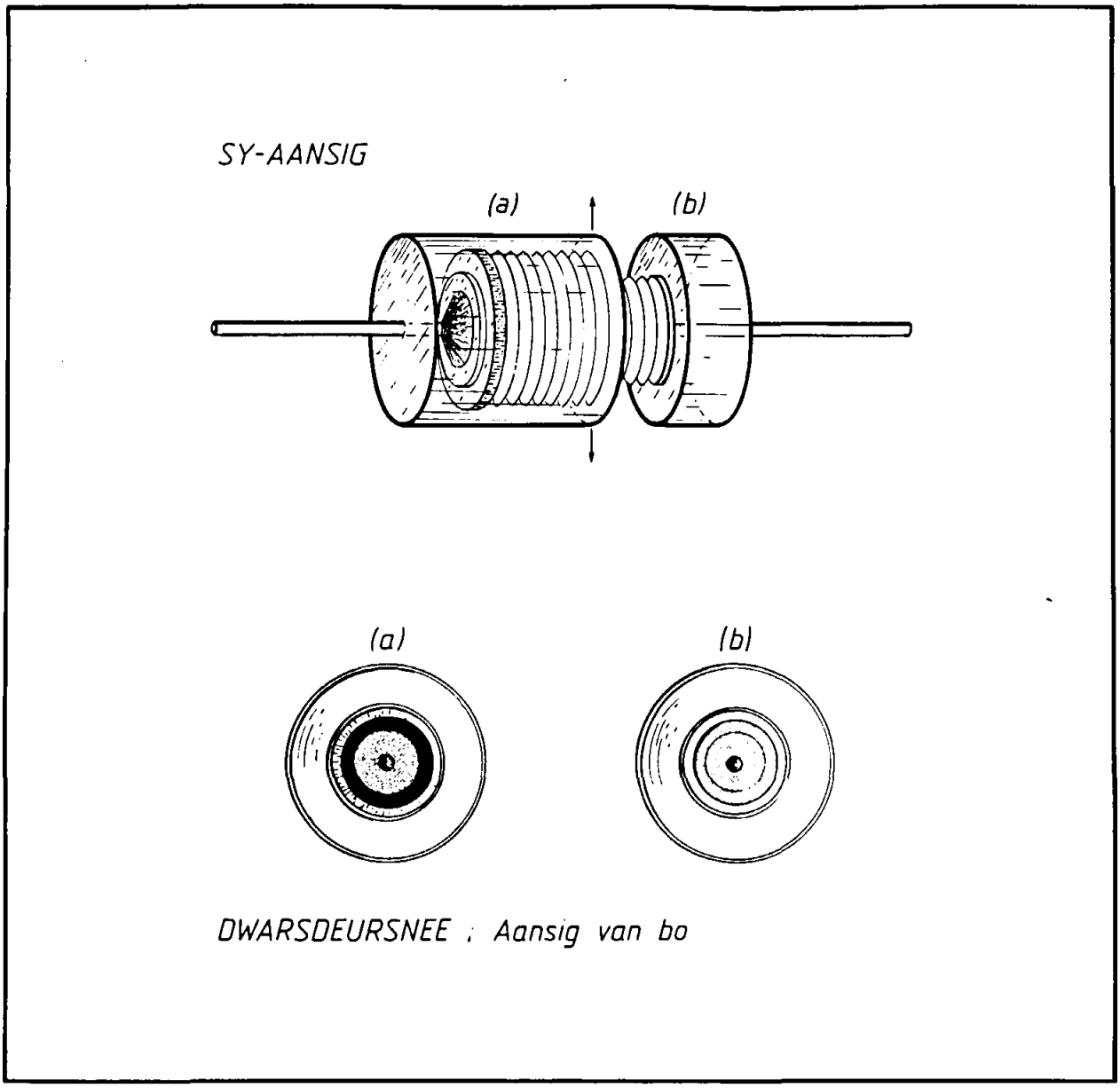
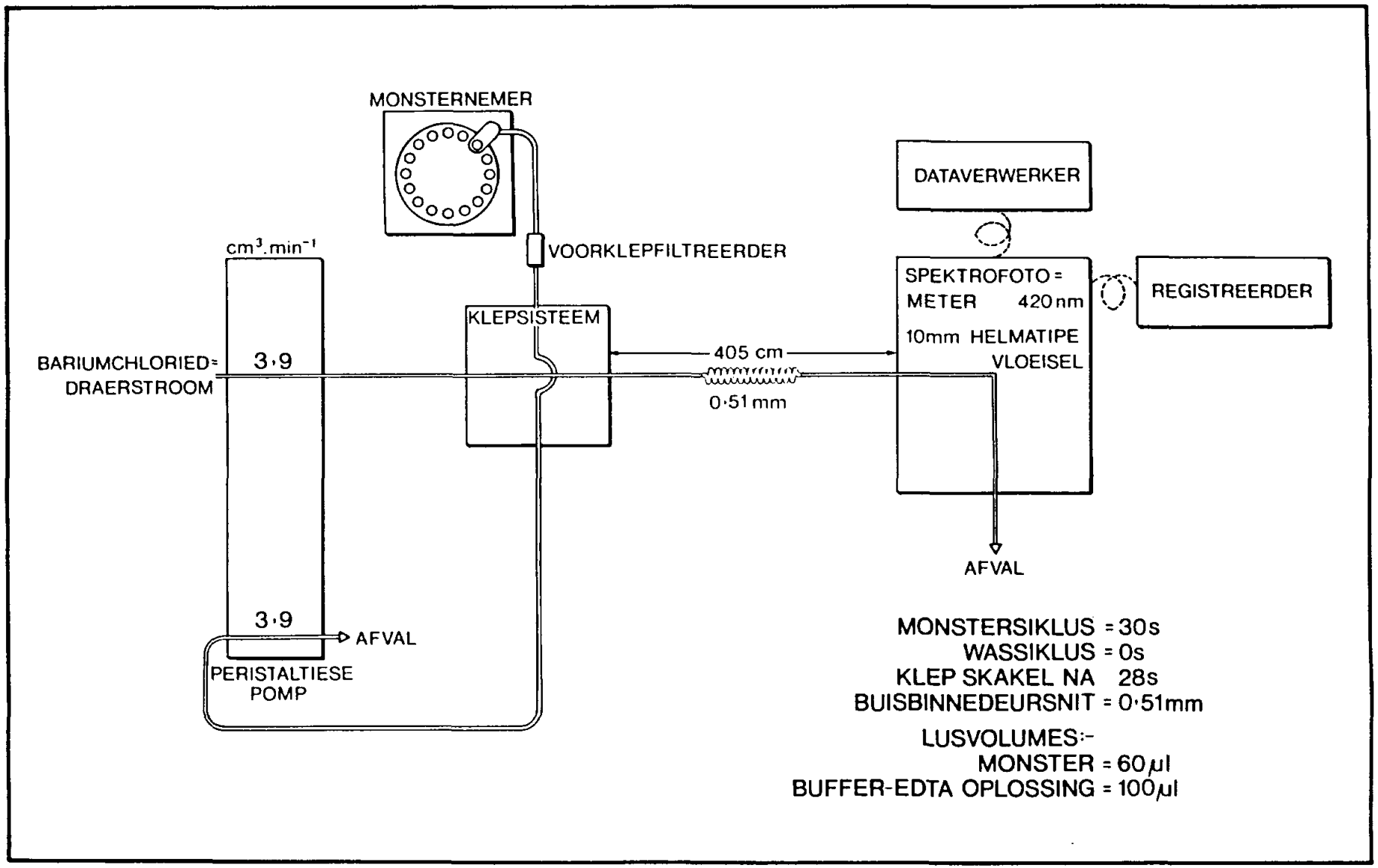


FIGUUR 1:

Skematiese voorstelling van die outomatiese voorklepfiltreersisteem met geaktiveerde koolstoffiltreerpapier.



FIGUUR 2:

Vloeidiagram vir sulfaat. Analisefrekwens 60 monsters per uur. Buislengte en -binnedeursnit word respektiewe= lik in cm en mm gegee.

BYLAAG 6

VLOEI-INSPUIT TURBIDIMETRIESE ANALISE VAN SULFAAT. DEEL 2. GEBRUIK VAN 'N ENKEL- OF DUBBELKANAALSISTEEM BY INDUSTRIËLE AFVALWATER.

J.F.VAN STADEN
Departement Chemie
Universiteit van Pretoria
PRETORIA

ABSTRACT

A simple, rapid single- and double channel flow-injection system for the determination of sulphate is described. The procedures are suitable for the analysis of sulphate in heavy coloured industrial effluents at a rate of up to 60 samples per hour with a coefficient of variation of better than 1%.

INLEIDING

Sekere watersisteme, veral industriële afvalwater en water vanuit mynhope, bevat komponente wat intens gekleurde oplossings met water vorm. Monsters van 'n soortgelyke aard kom ook voor in watersisteme wat gevoed word vanuit digbeboste gebiede in Suid-Afrika. Daar is gevind dat die kleurstowwe in bogenoemde monsters nie op die geaktiveerde koolstoffiltreerpapier adsorbeer nie. Gevolglik kan die kleur nie op hierdie wyse verwyder word nie. Bogenoemde monsters kom gewoonlik nie as 'n reël op 'n roetine basis in laboratoriums voor nie, maar verskyn soms wel as uitsonderings, gevolglik moet vir sulke monsters voorsiening gemaak word. Twee tipes vloeisisteme naamlik 'n analitiese enkel-, sowel as 'n dubbelkanaalsisteem is vir hierdie doel ontwikkel en aangepas.

By die enkelkanaalsisteem word die sulfaat in die gekleurde monsters saam met die steurings bepaal. 'n Blanko analise word dan outomaties op dieselfde reeks monsters uitgevoer. In die geval van die dubbelkanaalsisteem word 'n blankobepaling gelyktydig uitgevoer deur dieselfde monster met behulp van twee klepsisteme op dieselfde oomblik in twee analitiese kanale te voer na twee gekalibreerde deteksiesisteme.

EKSPERIMENTEEL

A. Enkelkanaalsisteem

Apparaat

Die instrumentasie wat in hierdie gedeelte gebruik word, is basies dieselfde as dié wat voorheen (Van Staden, 1982) beskryf is (Kyk Figuur 1).

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Reagense

Die voorbereiding van die bariumchloriedoplossing, bufferoplossing en die standaard sulfaatoplossing is volledig beskryf (Van Staden, 1982). Dit is egter nodig om bykomend 'n gelatienoplossing te berei. Dieselfde prosedure as by die bariumchloriedoplossing is van toepassing, behalwe dat die barium=chloried weggelaat word.

B. Dubbelkanaalsisteem

Apparaat

Die instrumentasie wat in hierdie gedeelte gebruik word, is basies dieselfde as dié wat voorheen (Van Staden, 1982) beskryf is, behalwe dat sommige gedu=pliseer word (kyk Figuur 2).

Reagense

Dieselfde reagense as by die enkelkanaalsisteem is van toepassing.

PROSEDURE

'n Skematiese diagram van die analitiese vloeisisteme verskyn in Figure 1 en 2. Die vermengingsisteme bestaan uit Tygonbuise met 'n binnedeursnee van 0,51 mm. Die buise is as vermengingspoele om 15 mm perspexstawe gedraai. Lynlengtes word in die figure aangedui.

Die volgende werkswyse word by die enkelkanaalsisteem gevolg.

Die sulfaat in 'n reeks gekleurde monsters word saam met die steurings op die gewone wyse bepaal met bariumchloried in die draerstroom. Monsters van 'n outo=matiese Cenco monsternemer word outomaties met behulp van 'n 60 µℓ monster=nemingslus in die draerstroom ingespuit deur gebruik te maak van 'n Carle mikro=

volume twee-posisie monsternemingsklep. Dit word afgewissel deur outomaties 100 µℓ van 'n alkaliese buffer-EDTA oplossing met die ander monsternemingslus in die draerstroom in te spuit. Die wyse waarop dit geskied is in bylaag 5 volledig beskryf.

'n Blanko analise word dan op dieselfde reeks monsters uitgevoer. Dit geskied deur dieselfde prosedure as hierbo te herhaal met slegs 'n gelatienoplossing, maar sonder 'n bariumchloriedoplossing in die draerstroom.

Die volgende werkswyse word by die dubbelkanaalsisteem gevolg.

Monsters, afgewissel met alkaliese buffer-EDTA oplossing, van 'n outomatiese Cenco monsternemer word deur die monsternemingslusse van twee verskillende klepsisteme met behulp van 'n peristaltiese pomp gepomp (kyk Figuur 2). Die twee klepsisteme spuit gelyktydig gelyke hoeveelhede in elk van die twee draerstrome. Op hierdie wyse word 60 µℓ monster in die analitiese kanaal met bariumchloriedoplossing as draerstroom ingelaat. Terselfdertyd word 60 µℓ in die blankokanaal met gelatienoplossing as draerstroom ingelaat. Dit word afgewissel deur outomaties 100 µℓ van 'n alkaliese buffer-EDTA oplossing met die alternatiewe monsternemingslusse in beide kanale in te spuit. Die wyse waarop dit geskied is volledig in bylaag 5 beskryf.

Om aanvaarbare pieke te verkry, is dit noodsaaklik dat beide die blanko- en analitiese kanale goed gesinchroniseer is. Verder moet die monsternemings= lusse en instrumentasie goed gekalibreer wees. Sinchronisering en kalibrasie kan met behulp van 'n verdunde gekleurde indikatoroplossing uitgevoer word.

RESULTATE EN BESPREKING

Die presisie en akkuraatheid van die voorgestelde VIA metode is getoets deur die resultate van 12 monsters te vergelyk met resultate wat met die vorige metode (in bylaag 7) verkry is nadat die monsters herhaaldelik behandel is.

Die standaardafwyking is minder as 1% op 14 toetse vir elke monster. Die resultate vergelyk gunstig (Tabel 1), behalwe vir die monsters waar die vorige metode heeltemal faal. Die t-distribusietoets (K. Eckschlager, 1969) is ook op bogenoemde metodes uitgevoer om te toets of die voorgestelde enkel- en dubbelkanaalsisteme geskik is vir toepassing in wateranalise. Die eksperimentele berekende t-waardes van 1,62 vir die enkel- en 1,66 vir die dubbelkanaalsisteme is kleiner as die getabuleerde t-waarde van 2,201 op die 95% betroubaarheidsinterval. Geen statisties betekenisvolle verskil kom op bogenoemde betroubaarheidsinterval voor nie, sodat die verskil in resultate te wyte is aan toevallige foute. Die voorgestelde sisteme is dus albei geskik vir die bepaling van sulfaat in water. Dit was verder ook nodig om die monsters herhaaldelik te sentrifugeer en te filtreer voordat die vorige metode (bylaag 7) wel toegepas kon word. Omdat die vorige metode soms gefaal het, was dit nodig om die akkuraatheid van die voorgestelde metode te toets deur bekende hoeveelhede sulfaat by die watermonsters te voeg en te bepaal hoeveel van die bygevoegde sulfaat herwin is. (Kyk tabel 2). Uit die resultate blyk dit dat die herwinbaarheid volgens hierdie prosedures respektiewelik gemiddeld 99,1% vir die enkelkanaal- en gemiddeld 98,8% vir die dubbelkanaalsisteem is. Willekeurige analises toon verder dat oordrag van een monster na 'n tweede weglaatbaar klein is. Geen basislynverskuiwing is ondervind nie.

ERKENNING

Hierdie projek is uitgevoer met finansiële ondersteuning van die Waternavorsingskommissie, die Wetenskaplike en Nywerheidsnavorsingsraad en die Universiteit van Pretoria.

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Van Staden, J.F. (1982). Automated Prevalve Sample Filtration in Flow Injection Analysis: Determination of Sulphate in Water Removing suspended solids and colour before sampling. Fresenius Z. Anal. Chem. 312, 438.

TABEL 1

Resultate van die presisie- en akkuraatheidstoets vir die voorgestelde VIA prosedures

Monster	VIA-metode alreeds beskryf Sulfaatkonsentrasie in $mg \cdot dm^{-3}$	Voorgestelde VIA pro= sedures Sulfaatkonsentrasie in $mg \cdot dm^{-3}$	Variasiekoëffisiënt[a] %
Enkelkanaalsisteem			
1	179	180	0,56
2	165	166	0,57
3	132	132	0,61
4	79	76	0,81
5	145	146	0,61
6	168	166	0,59
7	146	140	0,60
8	177	176	0,56
9	186	187	0,56
10	142	144	0,62
11	186	180	0,58
12	133	120	0,65
Dubbelkanaalsisteem			
1	179	178	0,56
2	165	167	0,56
3	132	131	0,60
4	79	77	0,79
5	145	146	0,60
6	168	166	0,58
7	146	141	0,61
8	177	177	0,56
9	186	186	0,59
10	142	144	0,60
11	186	179	0,56
12	133	117	0,66

[a] Vir 14 toetse op elke monster.

VIA = vloei-inspuitanalise

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TABEL 2:

Herwinningstoetse met die voorgestelde enkel- en dubbelkanaalsisteme op watermonsters met verskillende sulfaatkonsentrasies.

Monster	Sulfaatkonsentrasie in watermonster $mg \cdot dm^{-3}$	Herwinningstoets		
		Sulfaat bygevoeg mg	Sulfaat herwin mg	% Herwin
Enkelkanaalsisteem				
1	187	5	4,96	99,2
		10	9,92	99,2
		15	15,01	100,0
2	121	5	4,89	97,8
		10	9,88	98,8
		15	14,91	99,4
Gemiddelde % herwinning = 99,1				
Dubbelkanaalsisteem				
1	193	5	4,92	98,4
		10	9,90	99,0
		15	14,97	99,8
2	116	5	4,88	97,6
		10	9,85	98,5
		15	14,94	99,6
Gemiddelde % herwinning = 98,8				

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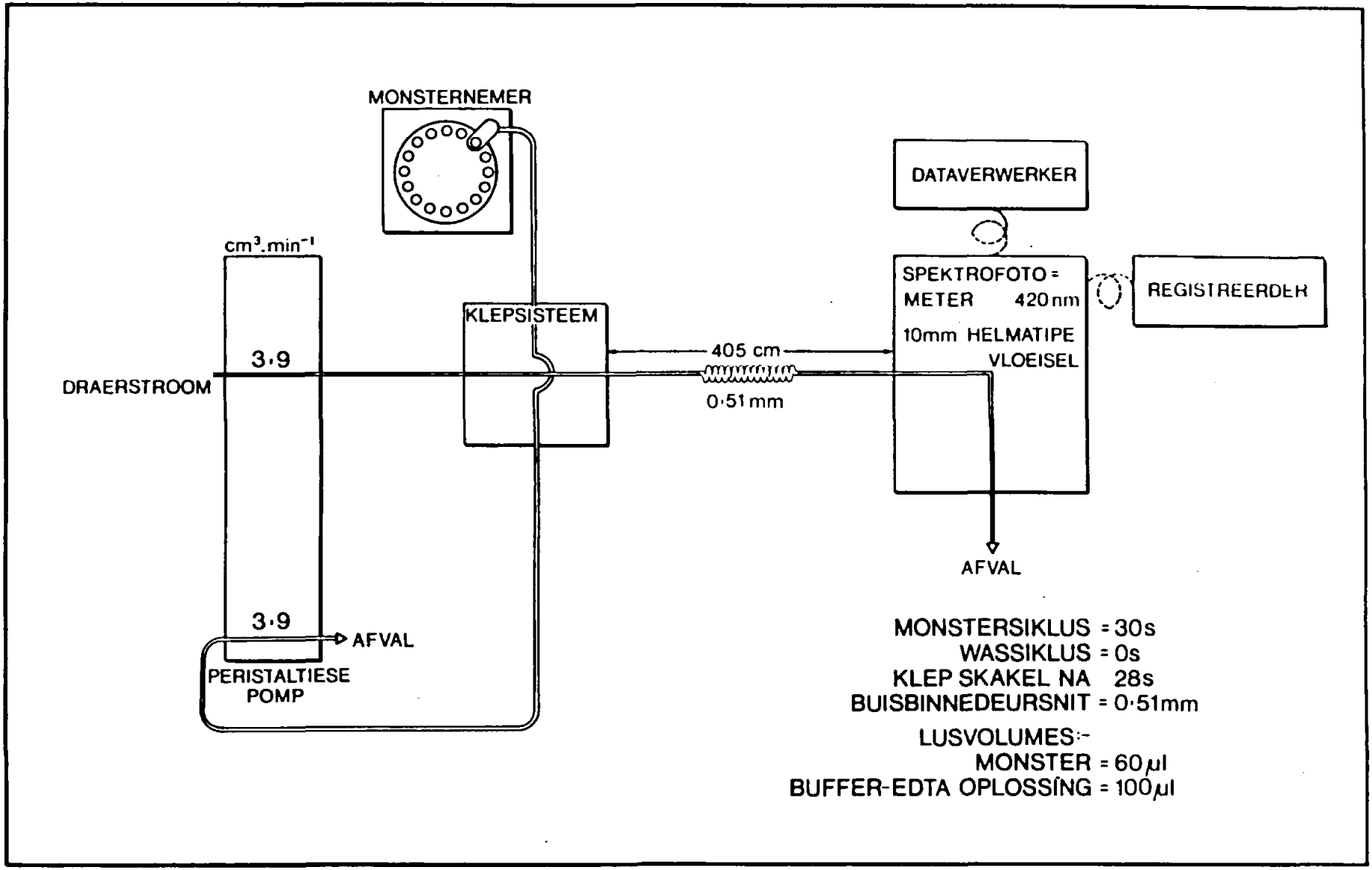
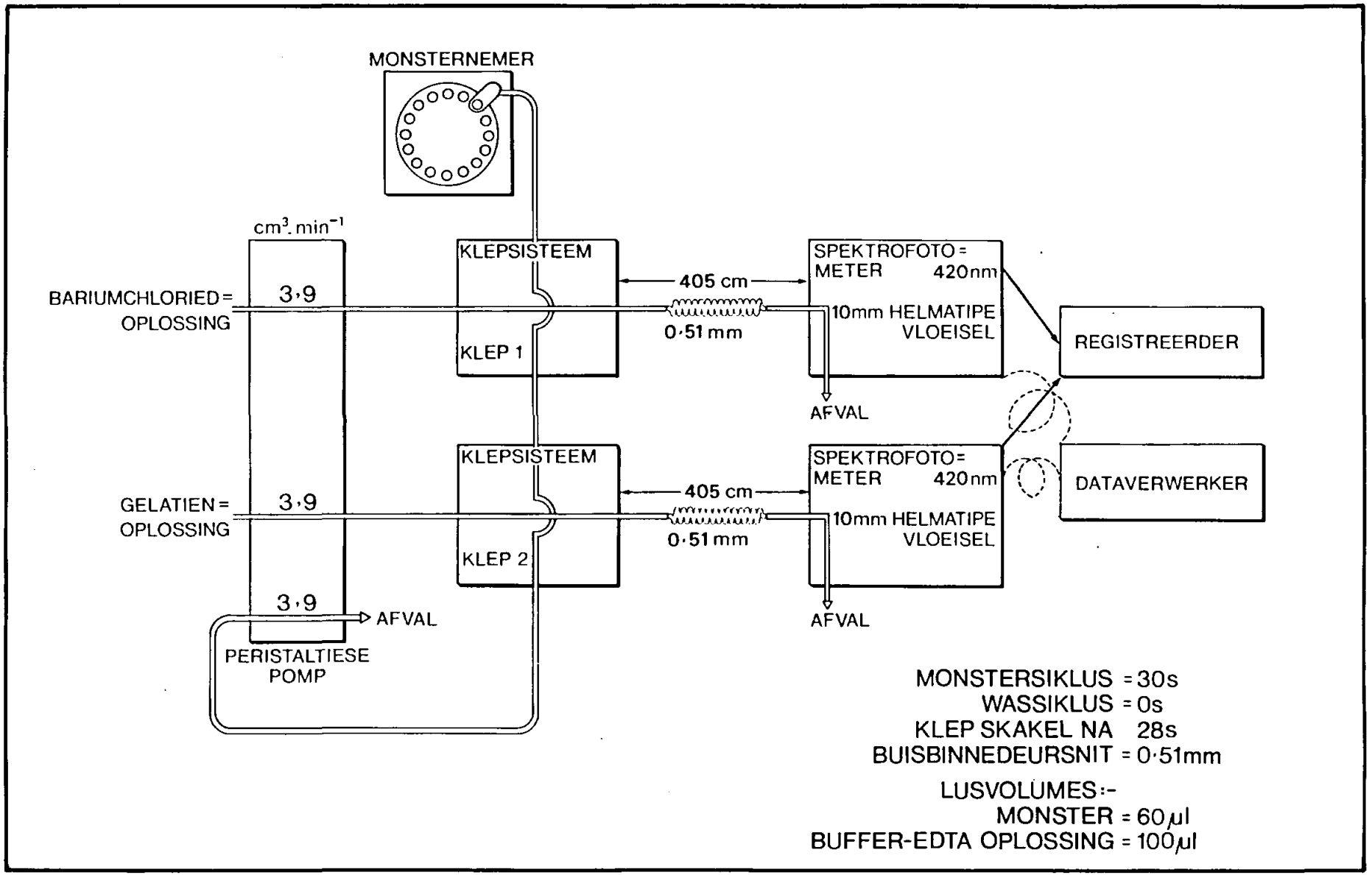


FIGUUR 1:

Enkelkanaalsisteem. Buislengte en -binnedeursnit word respektiewelik in cm en mm gegee.



FIGUUR 2:

Dubbelkanaalsisteem. Buislengte en -binnedeursnit word respektiewelik in cm en mm gegee.

BYLAAG 7

VLOEI-INSPUIT TURBIDIMETRIESE ANALISE VAN SULFAAT. DEEL 3. BEPALING VAN HOË SULFAATINHOUD IN INDUSTRIËLE AFVALWATER

J.F. van Staden
Departement Chemie
Universiteit van Pretoria
PRETORIA 0002

ABSTRACT

An automated flow-injection, turbidimetric procedure for the analysis of samples with a high sulphate content is described. The method is suitable for the analysis of sulphate in industrial effluent at a rate of up to 120 samples per hour with a coefficient of variation of better than 1%.

INLEIDING:

Enkele monsters, veral dié vanaf industriële afvalwater vanuit aanlegte waarin swaelsuur gebruik word, se sulfaatinhoud is relatief hoog sodat dit buite die konsentrasiegebied van bestaande metodes val. Hierdie monsters moet met die hand verdun word voordat die sulfaat in die verdunde monsters dan bepaal kan word volgens bestaande prosedures. Bogenoemde handverdunnings= metode neem egter baie tyd in beslag en dit kan verder ook lei tot 'n ver= laging in akkuraatheid en presisie van resultate.

Outomatiese dialise van monsters het verder die volgende voordele wat geïmplimenteer is in 'n metode:

(a) Steuringsmateriaal soos gesuspendeerde deeltjies en organiese kleur word outomaties verwyder.
(b) Verdunning van monsters vind outomaties plaas. Dit skakel sleurwerk uit.
(c) Geen verlies in akkuraatheid en presisie kom voor weens verdunning nie, want elke standaard en monster word onderwerp aan dieselfde konstante vloeidinamika.
(d) Produktiwiteit word verhoog.

EKSPERIMENTEEL:

Instrumentasie

Dialiseerder

'n 160 x 30 x 25 mm module gemasjieneer van perspex met 'n 0,50 mm radiaaldiepte groef word in die analitiese kanaal ingesluit vir outomatiese verdunning. (Kyk Figuur 1). Die dialiseereenheid is toegerus met 'n "Technicon Pre-mount Dialysis Membrane Type C".

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Dieselfde monsternemingsklep, monsternemer en spektrofotometer met deurvloei= sel as voorheen is gebruik. 'n Cenco peristaltiese pomp wat teen 30 revolusies per minuut funksioneer is egter gebruik. Die vermengingsisteem verskil ook met die insluiting van 'n dialiseerder asook wat die analitiese kanale betref.

Reagense

Analities reagens graad reagense is gebruik, tensy dit anders gespesifiseer is.

(i) Soutsuuroplossing

0,01 mol·dm^{-3} HCℓ. Los 80 cm^3 gekonsentreerde soutsuur (soortlike gewig = 1,19; pro analysi - Merck) in 500 cm^3 gedistilleerde water op. Verdun kwantitatief na 1 dm^3 met gedistilleerde water. Dit lewer 'n 1,00 mol·dm^{-3} stam-soutsuuroplossing. Berei 'n geskikte werkoplos= sing met 'n konsentrasie van 0,01 mol·dm^{-3} deur verdunning van 'n geskikte alikwot van die stamoplossing.

(ii) Bariumchloriedoplossing

Los 0,20 g timolkristalle op in 500 cm^3 gedistilleerde water by 'n temperatuur van ongeveer 80°C. Koel af tot 40°C. Verdun kwantitatief tot 2 dm^3 met gedistilleerde water. Voeg 4 g gelatien stadig by. Skud baie goed totdat alles opgelos het. Voeg 50 g bariumchloried= dihidraat ($BaC\ell_2 \cdot 2H_2O$) by en los op. Filtreer, indien nodig.

Standaarde

(i) Stam-sulfaatoplossing

Los 27,5112 g $(NH_4)_2SO_4$ op in gedistilleerde water en verdun kwantitatief na 1 dm^3. Die oplossing bevat 20 000 mg·dm^{-3} sul= faat as SO_4^{2-}.

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(ii) Standaard-sulfaatwerkoplossings

Berei die volgende reeks standaardwerkoplossings in 250 cm^3 volumetriese flesse.

Nommer	Volume stamoplossing (cm^3)	Sulfaatkonsentrasie in $mg.dm^{-3}$
1	20	1 600
2	30	2 400
3	40	3 200
4	50	4 000
5	60	4 800
6	75	6 000

PROSEDURE

'n Skematiese diagram van die analitiese vloeisisteem wat bedryf word in die bepaling van sulfaat verskyn in Figuur 1. Die vermengingsisteem bestaan uit Tygonbuise met lynlengtes en buisbinnedeursneë soos aangedui in die Figuur.

Die monsters vanaf die Cenco monsternemer word outomaties in die analitiese kanaal met behulp van 'n 200 µℓ monsternemingslus ingespuit. 'n 30 sekonde monsternemingsiklus word tussen opeenvolgende monsters gehandhaaf. Dit gee 'n kapasiteit van 120 monsters per uur. Die monsternemingsklepsisteem skakel elke 28 sekondes nadat die monsternemer na die volgende monster beweeg het. Die klepsisteem is gesinchroniseer met die monsternemingseenheid.

RESULTATE EN BESPREKING

'n Tipiese strookkaart registreerder uitdruk teen 'n monsternemingstempo van 120 monsters per uur verskyn in Figuur 2. Die kalibrasiekurwe is lineêr van 1 600 tot 6 000 $mg \cdot dm^{-3}$ (Figuur 3).

Die presisie en akkuraatheid van die voorgestelde vloei-inspuitprosedure word in Tabel 1 aangetoon. Die standaardafwyking is minder as 1% op 15 toetse vir elke monster. Die akkuraatheid van die voorgestelde VIA metode is getoets deur die resultate van 10 monsters te vergelyk met die resultate wat met die vorige metode in bylaag 7 verkry is waar die monsters met die hand verdun is voor analise. Die t-distribusietoets (K. Eckschlager, 1969) is ook op boge= noemde metodes uitgevoer om te toets of die voorgestelde vloei-inspuitprose= dure geskik is vir toepassing in wateranalise. Daar is gevind dat die eksperi= mentele berekende t-waarde van 1,31 kleiner is as die getabuleerde t-waarde van 2,262 op die 95% betroubaarheidsinterval. Daar is dus geen statisties betekenisvolle verskil op bogenoemde betroubaarheidsinterval nie. Die verskil in resultate kan verduidelik word aan die hand van toevallige foute sodat die voorgestelde VIA-metode dus geskik is. Die akkuraatheid van die voorgestelde metode is ook getoets deur bekende hoeveelhede sulfaat by watermonsters te voeg en te bepaal hoeveel van die bygevoegde sulfaat herwin is (Tabel 2). Die herwinbaarheid volgens hierdie metode is 97,5%.

ERKENNING

Hierdie projek is uitgevoer met finansiële ondersteuning van die Waternavor= singskommissie, die Wetenskaplike en Nywerheidsnavorsingsraad en die Universiteit van Pretoria.

VERWYSINGS

Eckschlager, K. (1969) in "Errors, Measurement and Results in Chemical Analysis", Hoofstuk 4, Van Nostrand, London, p. 107.

Van Staden, J.F. (1982). Automated Turbidimetric Determination of Sulphate in Surface, Ground and Domestic Water by Flow-Injection Analysis. Fresenius Z. Anal. Chem. 310, 239.

Van Staden, J.F. (1982). Automated Prevalve Sample Filtration in Flow Injection Analysis: Determination of Sulphate in Water Removing suspended solids and colour before sampling. Fresenius Z. Anal. Chem. 312, 438.

7 / ...

TABEL 1

Resultate van die presisie en akkuraatheidstoets vir die voorgestelde prosedure

Monster	VIA-metode alreeds beskryf Sulfaatkonsentrasie in $mg \cdot dm^{-3}$	Voorgestelde VIA-metode Sulfaatkonsentrasie in $mg \cdot dm^{-3}$	Variasiekoëffisiënt[a] %
1	1 950	1 936	0,78
2	3 437	3 451	0,76
3	1 921	1 907	1,03
4	4 071	4 083	0,71
5	1 769	1 760	0,84
6	1 606	1 632	0,97
7	5 130	5 146	0,69
8	4 381	4 370	0,70
9	3 967	3 989	0,77
10	4 206	4 237	0,70

[a]Vir 15 toetse op elke monster

VIA = vloei-inspuitanalise

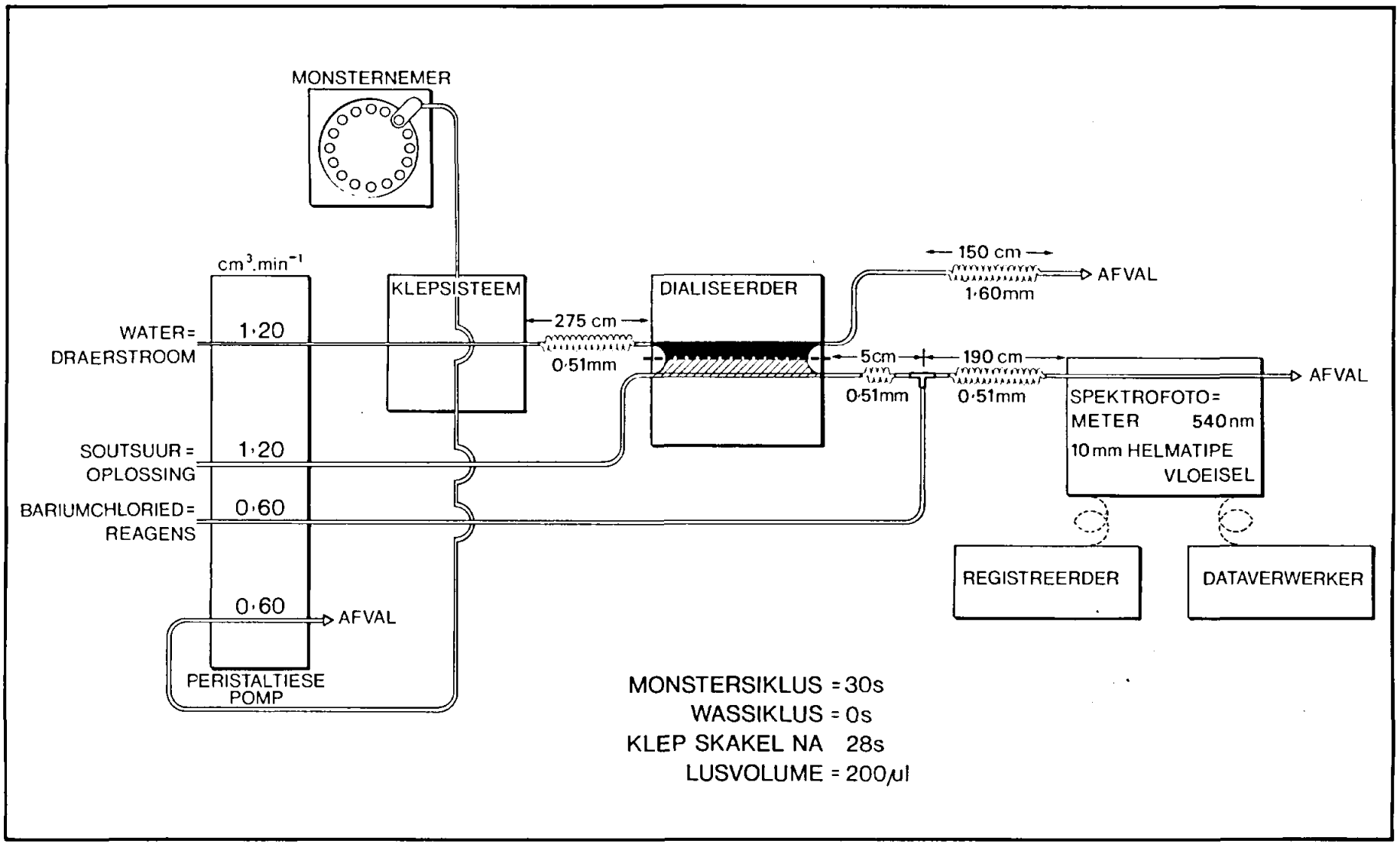
TABEL 2

Herwinningstoetse met die voorgestelde VIA metode op watermonsters met verskillende sulfaatkonsentrasies

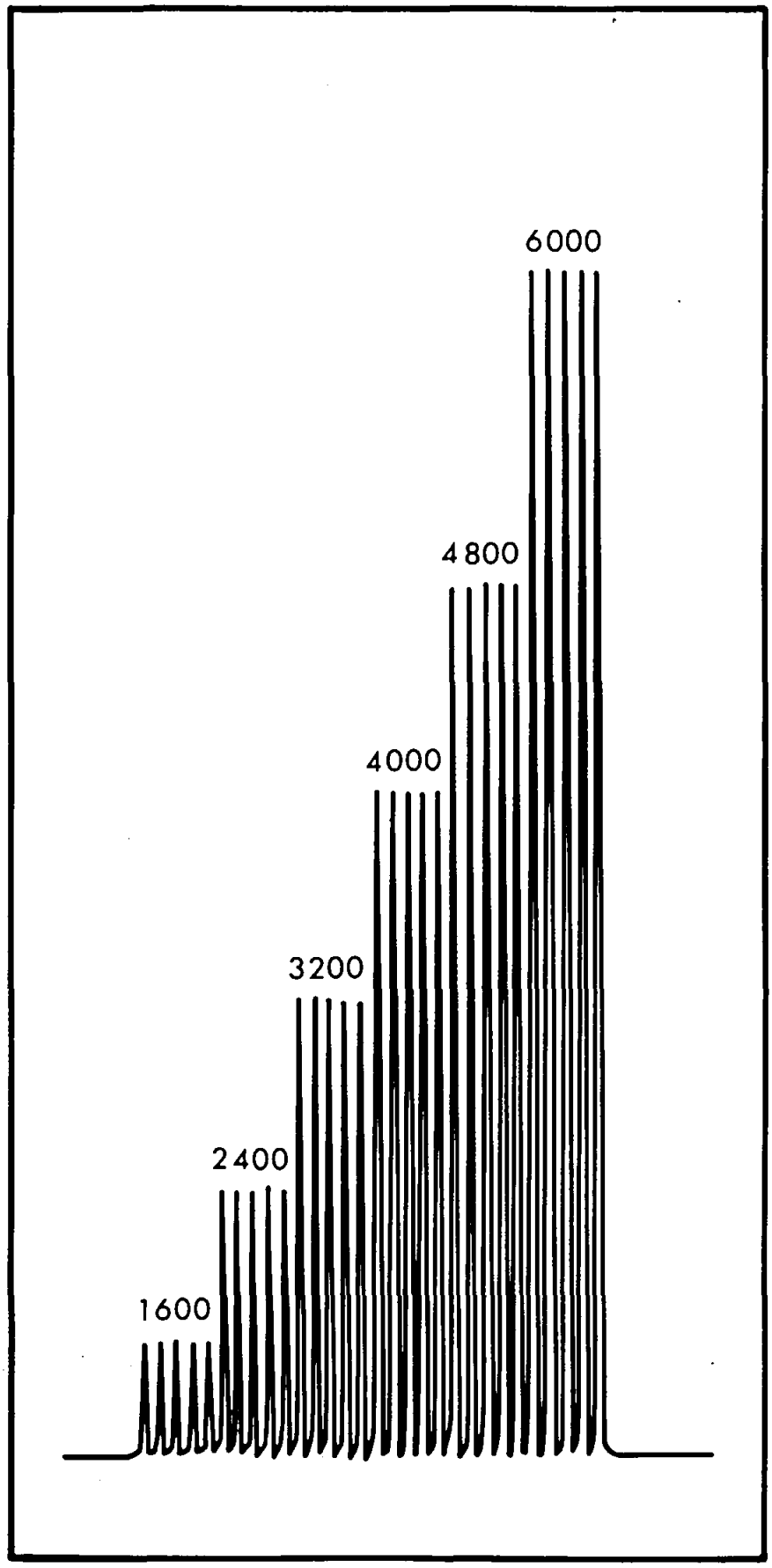
Monster	Sulfaatkonsentrasie in watermonster $mg \cdot dm^{-3}$	Herwinningstoets		
		Sulfaat bygevoeg mg	Sulfaat bygevoeg mg	% herwin
1	1 690	50	48	96
		100	98	98
2	4 735	50	49	98
		100	98	98

Gemiddelde % herwinning = 97,5

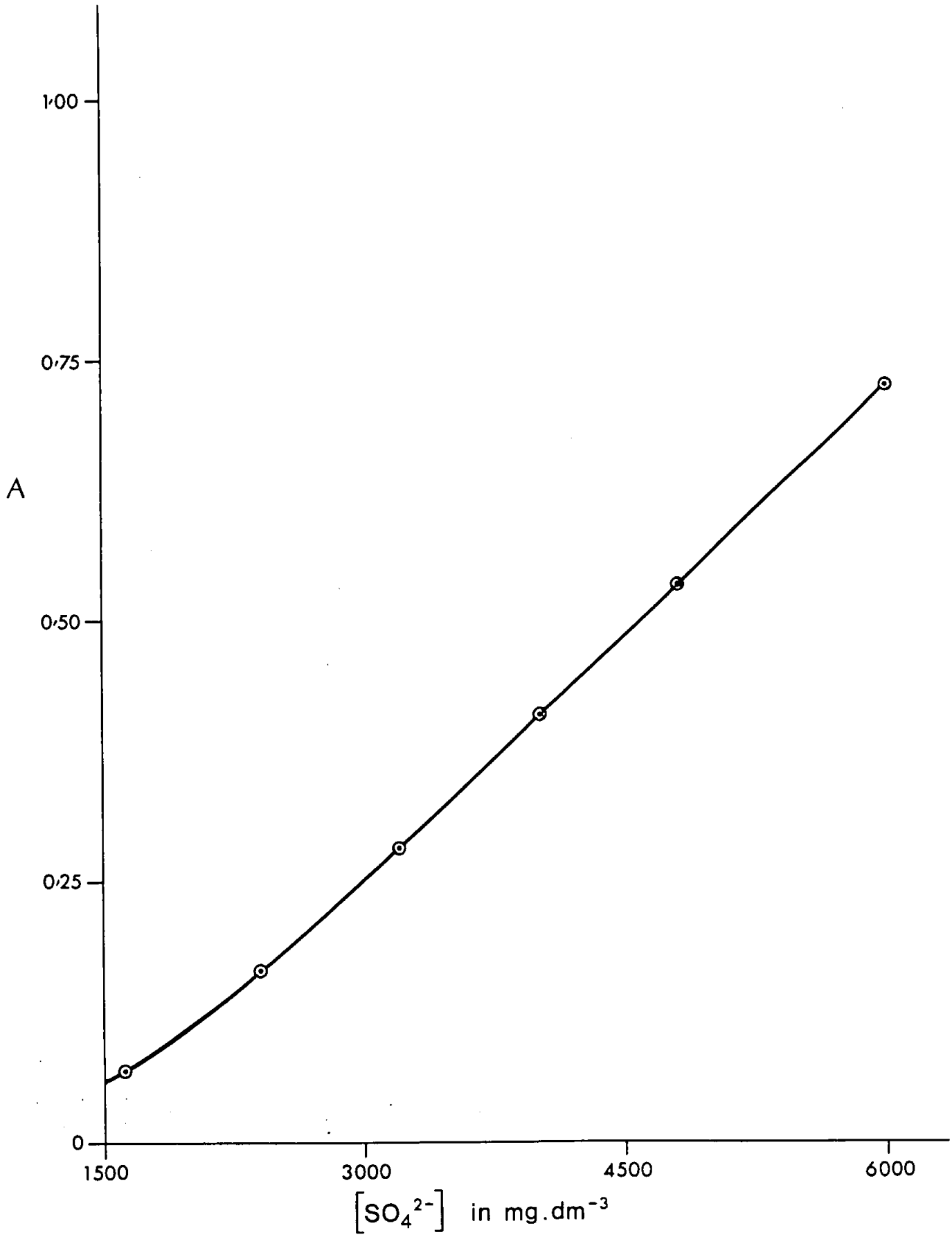
VIA = vloei-inspuitanalise



FIGUUR 1: Analitiese vloeisisteem. Analisefrekwens 120 monsters per uur. Buislengte en -binnedeursnit word respektiewelik in cm en mm gegee.



FIGUUR 2: Tipiese registreerder strookkaart. Die getal= le op die pieke dui sulfaatkonsentrasie as $mg.dm^{-3}$ aan.



FIGUUR 3: Kalibrasiekurwe

BYLAAG 8

INDIREKTE BEPALING VAN SULFAAT DEUR DIREKTE METING MET 'N LOODIOONSELEKTIEWE ELEKTRODE

J F van Staden
Departement Chemie
Universiteit van Pretoria
0002

ABSTRACT

A manual procedure for the indirect determination of sulphate by direct measurement with a lead ionselective electrode is described. An excess of lead(II)ions is added to the sample solution containing sodium perchlorate as ionic strength adjustor and methanol-formaldehyde to decrease the solu= bility and retard oxidation of the membrane. The system is useful for routine sulphate analysis in the range 20-200 $mg \cdot dm^{-3}$ with a reproducibility of ± 5%. Major interference is caused by cations (Cu^{2+}, Hg^{2+}, Ag^{+}) and anions which form insoluble lead salts (PO_4^{3-}). The effects of ionic strength adjustors, lead(II) salts used, organic solvents and the interferences of cations and anions are discussed.

INLEIDING

Die turbidimetriese spektrofotometriese bepaling van sulfaat word tans nog steeds in die meeste roetine laboratoriums gebruik vir sulfaatanalises. Kleur en troebelrigheid in sommige watermonsters steur egter by bogenoemde metodes. Hierdie steurings kan wel uitgeskakel word deur outomatiese voorklepfiltrasie met geaktiveerde koolstoffiltreerpapier, 'n dubbelkanaalsisteem of deur dialise (Van Staden 1982, 1984). Daar bestaan egter 'n paar monsters waar bogenoemde tegnieke nie so geslaagd is nie.

By elektrometriese (potensiometriese) titrasies met behulp van 'n ioonselektiewe elektrode is bogenoemde steurings nie 'n faktor nie. Potensiometriese metings vir die bepaling van sulfaat met ioonselektiewe elektrodes word gewoonlik uitgevoer deur 'n presipitasietitrasie met 'n lood(II)oplossing en gemeet met 'n loodioonselektiewe elektrode. (Orion Research, 1981, 1982).

Ross en Frant (1969) het aanvanklik 'n metode beskryf vir die potensiometriese titrasie van sulfaat met loodperchloraat waar die meting geskied het met behulp van 'n loodioonselektiewe elektrode. Die metode is verskeie kere verbeter en gemodifiseer, totdat daar tans 'n aanvaarbare prosedure (Orion, 1981, 1982) is wat gebruik word. Bogenoemde metode berus egter op 'n titrimetriese prosedure wat tydrowend is. Gevolglik is ondersoek ingestel na die moontlikheid om sulfaat indirek te bepaal deur direkte meting sonder om te titreer.

EKSPERIMENTEEL

APPARAAT

Potensiometriese metings is uitgevoer met 'n Orion Model 901 digitale Ionalyzer. Die sulfaat is indirek bepaal deur die lood(II)ioonaktiwiteite met behulp van 'n Orion Model 94-82 vaste membraan loodioonselektiewe elektrode te meet. Bogenoemde elektrode se membraanfase bestaan uit 'n PbS/Ag_2S mengsel in die vaste vorm. 'n Orion Model 90-02 verwysingselektrode met 'n dubbele aansluiting is gebruik. Die buitenste kamer is gevul met 'n versadigde oplossing van kaliumchloried en 'n hoeveelheid metanol wat dieselfde is as die hoeveelheid wat in die monsters gebruik is.

REAGENSE

Analities reagens-graad reagense is gebruik, tensy dit anders gespesifiseer is.

(i) Ioonsterkte verstelbare oplossing (ISA).

Los 140,46 g $NaC\ell O_4 \cdot H_2O$ in gedistilleerde water op en verdun kwantitatief na 200 cm^3.

STANDAARDE

(i) Stam-loodperchloraatoplossing

Voeg 10,7737 g lood(II)oksied by 500 cm^3 gedistilleerde water in 'n 2 dm^3 volumetriese fles. Voeg hierby drupsgewys perchloorsuur en skud goed. Herhaal totdat alle lood(II)oksied opgelos het. Verdun kwantitatief tot by die merk. Hierdie oplossing is ekwivalent aan 'n oplossing wat 5000 mg Pb^{2+} in 1 dm^3 bevat.

(ii) Standaard-lood(II)oplossing

Verdun 180 cm^3 van bogenoemde standaard loodperchloraatoplossing kwantitatief na 1 dm^3 met gedistilleerde water. Hierdie oplossing bevat 900 $mg \cdot dm^{-3}$ Pb^{2+}.

(iii) Stam-sulfaatoplossing

Los 2,9574 g watervrye natriumsulfaat, gedroog by 120° C vir 2 uur, op in gedistilleerde water en verdun kwantitatief na 2 dm^3. Stoor in 'n poli-etileen-houer by 4° C. Die oplossing bevat 1000 $mg \cdot dm^{-3}$ sulfaat as SO_4^{2-}.

(iv) Standaard-sulfaatwerkoplossings

Berei die volgende reeks standaardoplossings in 1 dm^3 volumetriese flesse.

Nommer	Volume stamoplossing (cm^3)	Sulfaatkonsentrasie in $mg \cdot dm^{-3}$
1	20	20
2	40	40
3	60	60
4	80	80
5	100	100
6	120	120
7	140	140
8	160	160
9	180	180
10	200	200

PROSEDURE

Pipetteer 50 cm^3 monster in 'n 250 cm^3 beker. Voeg 2 cm^3 ISA, 25 cm^3 900 $mg \cdot dm^{-3}$ Pb^{2+}-oplossing en 25 cm^3 van die metanol-formaldehiedoplossing by. Metings word uitgevoer terwyl die oplossing teen 'n konstante tempo geroer word met 'n Teflon-bedekte magnetiese roerder.

Kalibrasie word uitgevoer deur die 50 cm^3 monsterhoeveelheid te vervang met 50 cm^3 van die standaard sulfaatoplossings vir elke meting.

RESULTATE EN BESPREKING

Verskeie veranderlikes beïnvloed die resultate in hierdie bepaling. Gevolglik is besluit om hierdie veranderlikes deeglik te evalueer in die optimisering van die prosedure.

Die elektrode bepaal primêr die vry Pb^{2+}-ione in oplossing. Sulfaatione kan dus indirek bepaal word deur 'n oormaat Pb^{2+}-ione by die sulfaat te voeg en die resulterende hoeveelheid vry Pb^{2+}-ione te meet. Die oormaat Pb^{2+}-ione kan as 'n oplossing van loodnitraat of loodperchloraat bygevoeg word. Ross en Frant (1969) en Orion (1981, 1982) gebruik loodperchloraat in die onderskeie titrasiesisteme terwyl Scheide en Durst (1977) loodnitraat verkies het. Beide sisteme is volledig geëvalueer op die voorgestelde metode. Daar is gevind dat 'n oplossing van loodperchloraat beter resultate lewer. Die prosedure met loodnitraat het die volgende knelpunte gelewer. Die elektrode was meer onstabiel by lae sulfaatkonsentrasies, die kurwe by lae sulfaatkonsentrasies het vinniger afgeplat en steurings het 'n groter invloed uitgeoefen.

Natriumperchloraat word as ioonsterkte versteller in die prosedure gebruik. Die voorgestelde konsentrasie van 0,10 $mol \cdot dm^{-3}$ natriumperchloraatoplossing

(Orion, 1981, 1982) in die finale oplossing het bevredigende resultate verskaf en dit is net so in die voorgestelde prosedure geïnkorporeer. Daar is egter gevind dat sodra die soutinhoud in die monster te hoog sou word soos met seewater, bogenoemde konsentrasie aangepas moet word om wisselende ioonsterktes uit te skakel. Kaliumperchloraat is min oplosbaar in water. Dit skakel hierdie stof outomaties as ioonsterkte versteller uit.

Die relatiewe hoë oplosbaarheid van $PbSO_4$ (K_{sp} = 1,6 x 10^{-8}) in waterige medium kan 'n beperkende invloed op die indirekte bepaling van sulfaat uitoefen, veral by lae sulfaatkonsentrasies. Dit bring mee dat die volgende knelpunte ondervind word. Die elektrode is onstabiel en die kurwe plat vinniger af. Presipitaatvorming vind ook stadiger plaas. Verder is gevind dat die vorm van die kurwe van so 'n aard is dat baie swak presisie verkry word.

Ross en Frant (1969), Rechnitz en Kenny (1970), Scheide en Durst (1977) en Orion (1981, 1982) het verskeie organiese nie-waterige oplosmiddels gebruik om die oplosbaarheid van die $PbSO_4$-presipitaat te verlaag. Selig en Salomon (1974) het gevind dat p-dioksaan soos aanbeveel deur Ross en Frant (1969) nie geskik is as 'n nie-waterige sisteem nie. p-Dioksaan vorm peroksiedes in lug en die gevormde peroksied vergiftig die elektrode selfs in lae hoeveelhede. Dit is nie prakties uitvoerbaar om net vars oopgemaakte bottels p-dioksaan (Selig en Salomon, 1974) te gebruik nie. Dit is te duur.

Voorlopige toetse het aangetoon dat die hoeveelhede en tipe organiese oplosmiddel 'n belangrike en kritiese faktor vorm by die helling van die kalibrasiekurwe van sulfaat. Rechnitz en Kenny (1970) het die invloed van verskeie organiese oplosmiddels ondersoek, terwyl Scheide en Durst (1977) 'n 80 persent

isopropanol-water mengsel aanbeveel het. Bogenoemde ondersoeke is egter uitgevoer deur indirekte titrasie van sulfaat. Verder het Rechnitz en Kenny (1970) die loodperchloraatsisteem gebruik, terwyl Scheide en Durst (1977) 'n loodnitraatoplossing gebruik het. Eersgenoemde se resultate berus op direkte potensiometriese metings van die lood(II)ioon in 'n reeks water-organiese mengsels. Die voorgestelde metode berus egter op die indirekte bepaling van sulfaat deur direkte meting. Gevolglik is ondersoek ingestel na die invloed van 'n aantal organiese oplosmiddels op die sulfaatkurwe. Die resultate word in Figuur 1 aangetoon. Die helling is dwarsdeur sub-Nernstian. Die invloed van die relatiewe hoë oplosbaarheid van $PbSO_4$ kan duidelik waargeneem word uit die kurwe waar die metings net in water uitgevoer is. Die beste werkskurwe word met metanol verkry.

Omdat die elektrode die oormaat vry Pb^{2+}-ione meet nadat presipitasie met sulfaatione plaasgevind het, moes vasgestel word watter hoeveelheid Pb^{2+}-ione aanvanklik bygevoeg moes word. Die resultate van hierdie ondersoek word in Figuur 2 aangetoon. Hieruit blyk dit duidelik dat kromme met die hoogste presisie oor die hele konsentrasiegebied verkry word met 'n 900 $mg \cdot dm^{-3}$ Pb^{2+}-ioonoplossing.

Orion (1981, 1982) gebruik 'n 50 persent metanol-formaldehiedoplossing om die oplosbaarheid van die $PbSO_4$-presipitaat te verlaag en om oksidasie van die elektrode te vertraag. Daar is gevind dat die voorgeskrewe drie druppels 37 persent formaldehied by 1000 cm^3 metanol wel die oksidasie van die membraan vertraag, maar dat 'n 25 persent metanol-formaldehiedoplossing in die finale oplossing heeltemal voldoende is in die bepaling.

Verskeie metodes is aangewend om die kalibrasiekromme nog verder te optimi= seer vir 'n hoër presisie, maar dit was onsuksesvol. 'n Kalibrasiekurwe van 'n reeks standaard sulfaatoplossings verskyn in Figuur 3.

Die resultate van die voorgestelde metode stem goed ooreen met die resultate wat verkry is met die standaard outomatiese gesegmenteerde en 'n vloei-inspuit analitiese metode (Tabel 1). Die relatiewe standaard afwyking vir die voorge= stelde metode is $\pm$ 5%. Die akkuraatheid van die voorgestelde metode is ook getoets deur bekende hoeveelhede sulfaat by watermonsters te voeg en te bepaal hoeveel van die bygevoegde sulfaat herwin is. (Tabel 2). Die herwin= baarheid volgens hierdie metode is gemiddeld 98%.

Die loodioonselektiewe elektrode is wel onderworpe aan steurings van Cu^{2+}-, Hg^{2+}- en Ag^{+}-ione. Hierdie ione vergiftig die elektrode vinnig en moenie in die monster aanwesig wees nie. (Orion, 1981, 1982). Daar is gevind dat die $HgC\ell_2$ wat gebruik word om watermonsters te preserveer, die elektrode baie vinnig vergiftig deurdat 'n lagie op die elektrode vorm. Die paar monsters wat probleme verskaf met die turbidimetriese prosedure, kan wel met die ioon= selektiewe prosedure bepaal word, mits dit dus nie met $HgC\ell_2$ gepreserveer word nie.

Fe^{3+}- en Cd^{2+}-ione beïnvloed ook die membraanoppervlakte. (Orion, 1981). Ondersoek het bevestig dat solank die Fe^{3+}- en Cd^{2+}-vlak nie die konsentrasie van die Pb^{2+}-ione in die finale oplossing oorskry nie, dit nie steur nie. Ca^{2+}-ione kan ook steur deurdat dit min oplosbare $CaSO_4$ vorm. $CaSO_4$ ($K_{sp} = 1{,}9 \times 10^{-4}$) is egter meer oplosbaar as $PbSO_4$ ($K_{sp} = 1{,}6 \times 10^{-8}$). Gevolglik behoort die steuring minimaal te wees. Verder behoort alle Ca^{2+}-ione wat mag steur alreeds gebind te wees as $CaSO_4$ in die monster. Ondersoek met

standaard sulfaatoplossings het aangetoon dat vir 'n 20 $mg \cdot dm^{-3}$ oplossing Ca^{2+}-ione steur indien die konsentrasie daarvan groter as 120 $mg \cdot dm^{-3}$ is. Vir 'n 100 $mg \cdot dm^{-3}$ sulfaatoplossing is egter gevind dat steuring wel voorkom indien die Ca^{2+}-ioonkonsentrasie 200 $mg \cdot dm^{-3}$ oorskry.

Anione wat minder oplosbare loodsoute as $PbSO_4$ vorm, moet afwesig wees. $Pb_3(PO_4)_2$ ($K_{sp} = 7,9 \times 10^{-43}$) is minder oplosbaar as $PbSO_4$. Ondersoek het aangetoon dat dit wel die geval is en dat vir 20 $mg \cdot dm^{-3}$ sulfaat die steuring meer merkbaar is as vir 100 $mg \cdot dm^{-3}$ sulfaat met 'n 20 $mg \cdot dm^{-3}$ fosfaatoplossing. Chloried-, nitraat- en waterstofkarbonaatione steur ook in die bepaling (Orion, 1981, 1982). Ondersoek het bevestig dat baie hoë konsentrasies wel kan steur.

GEVOLGTREKKINGS

Sulfaatkonsentrasies in oppervlakte-, grond- en huishoudelike water kan indirek deur direkte meting met 'n loodioonselektiewe elektrode bepaal word. Die voorgestelde metode is geskik vir die bepaling van sulfaat in die gebied 20 tot 200 $mg \cdot dm^{-3}$. Steurings word hoofsaaklik ondervind deur katione (Cu^{2+}, Hg^{2+}, Ag^{+}) wat die elektrode vergiftig, anione wat min oplosbare loodsoute vorm (PO_4^{3-}) en hoë konsentrasies chloried-, nitraat- en waterstofkarbonaatione. Alhoewel Ca^{2+}-, Fe^{3+}- en Cd^{2+}-ione ook kan steur, skep dit nie juis probleme nie.

ERKENNING

Hierdie projek is uitgevoer met finansiële ondersteuning van die Waternavorsingskommissie, die Wetenskaplike en Nywerheidsnavorsingsraad en die Universiteit van Pretoria.

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2. Orion Research, (1982). Handbook of Electrode Technology.

3. Rechnitz, G A and Kenny, N C (1970). Potentiometric measurements in aqueous, non-aqueous, and biological media using a lead ion-selective membrane electrode. Anal. Letters. 3 (1970) 259.

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9. Van Staden J F (1984) Vloei-inspuit turbidimetriese analise van sulfaat. Water SA.

TABEL 1

Vergelyking van die resultate verkry met 'n standaard outomatiese gesegmenteerde metode, 'n vloei-inspuit metode (VIA) en die voorgestelde loodioonselektiewe metode (ISE).

Monster	$[SO_4^{2-}]$as $mg \cdot dm^{-3}$			Variasiekoëffisiënt[a] %
	Gesegmenteerde metode	VIA	ISE	
1	198	192	197	2,8
2	181	177	176	3,1
3	143	147	140	3,4
4	103	106	102	4,1
5	43	39	40	4,9
6	85	87	88	4,4
7	70	64	69	4,6

[a]Vir 5 toetse in elke geval.

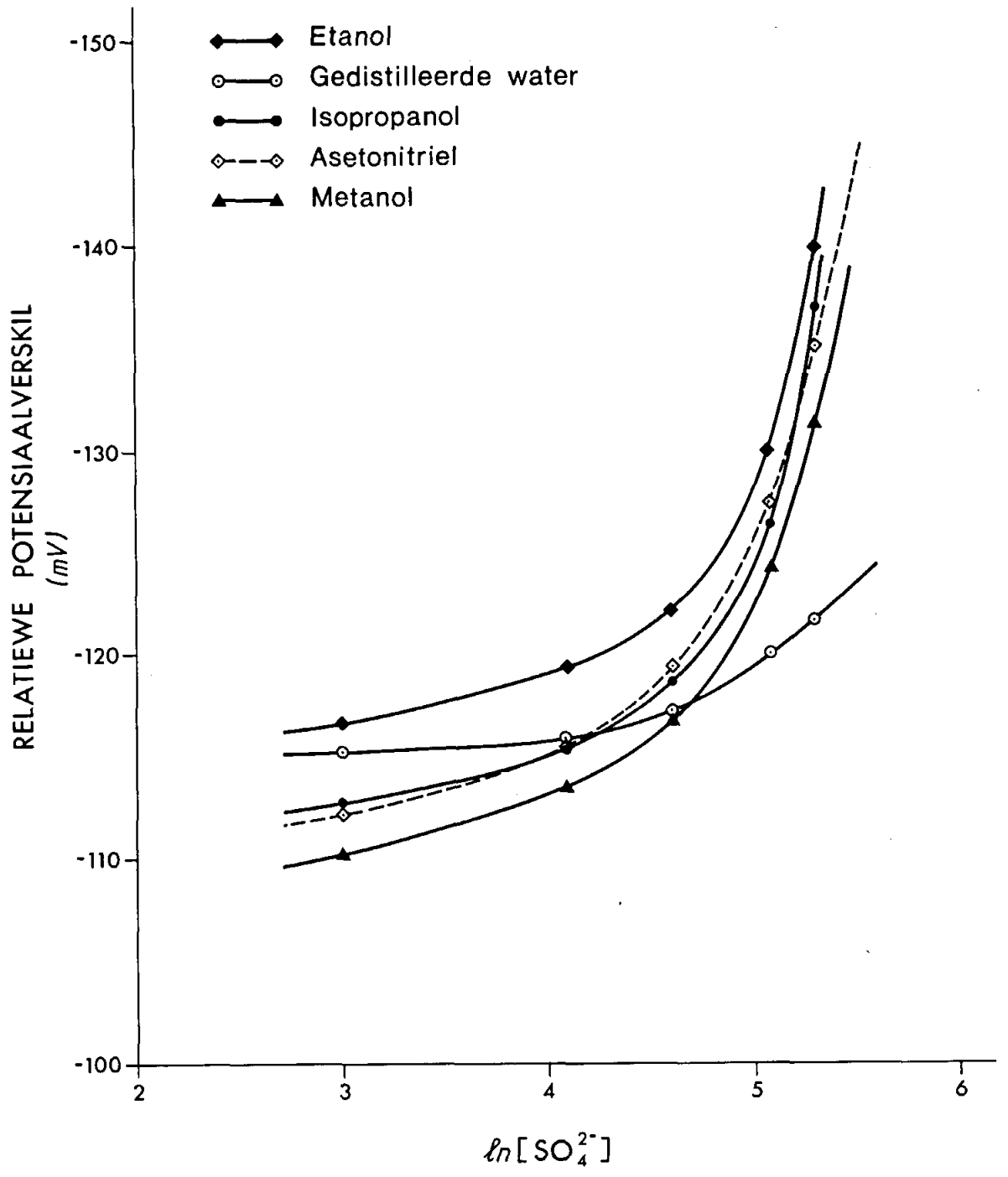
TABEL 2

Herwinningstoetse met die voorgestelde ISE metode op drie watermonsters met verskillende sulfaatioonkonsentrasies (alle waardes is die gemiddelde van triplikaatanalises)

Monster	$[SO_4^{2-}]$ in watermonster $mg \cdot dm^{-3}$	Herwinningstoets		
		SO_4^{2-} bygevoeg mg	SO_4^{2-} herwin mg	% Herwin
1	189	5,0	4,90	98,0
		10,0	9,85	98,5
		15,0	14,90	99,3
2	37	5,0	4,75	95,0
		10,0	9,80	98,0
		15,0	14,80	98,7
3	121	5,0	4,85	97,0
		10,0	9,85	98,5
		15,0	14,90	99,3

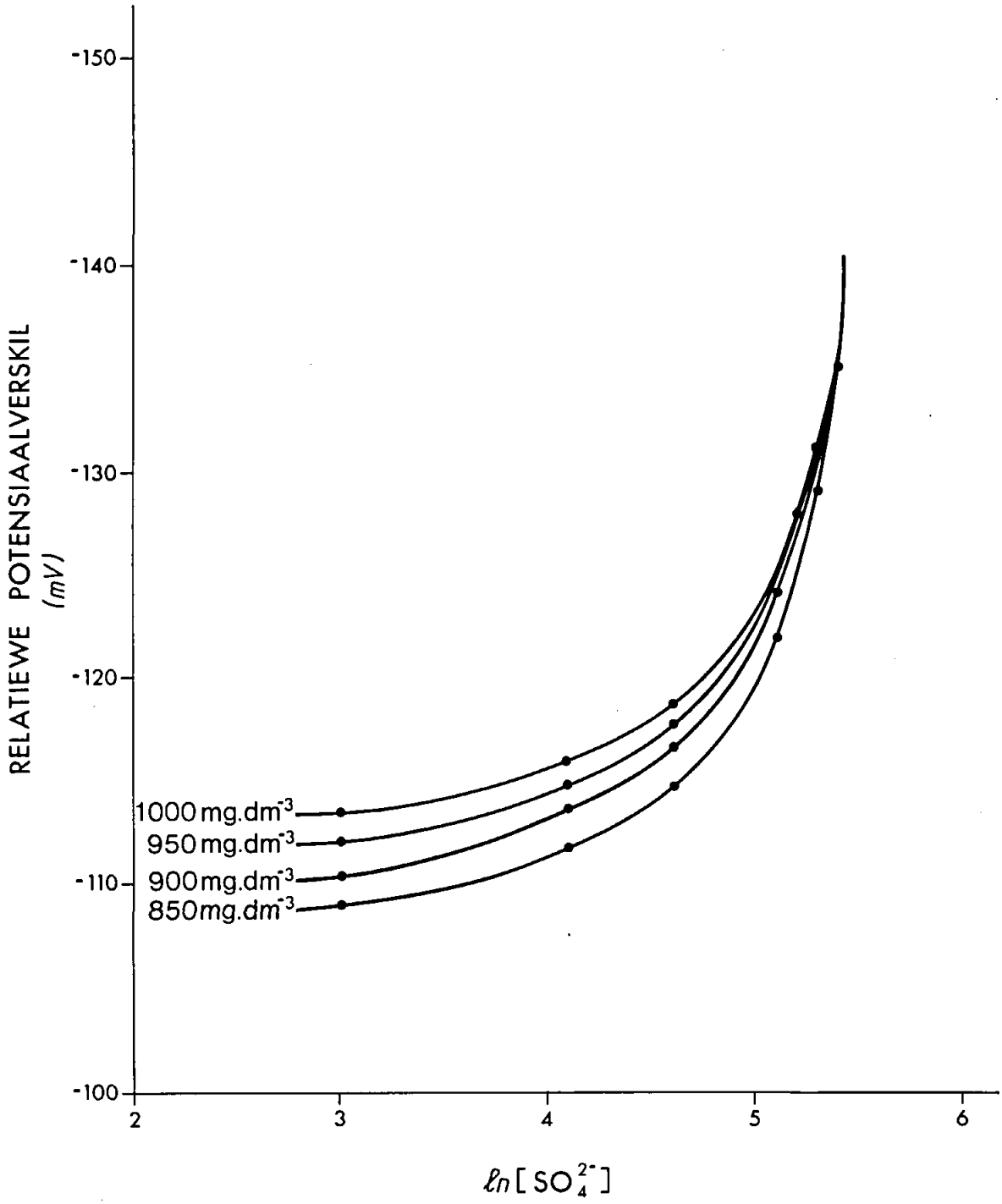
Gemiddelde % herwinning

= 98,0%



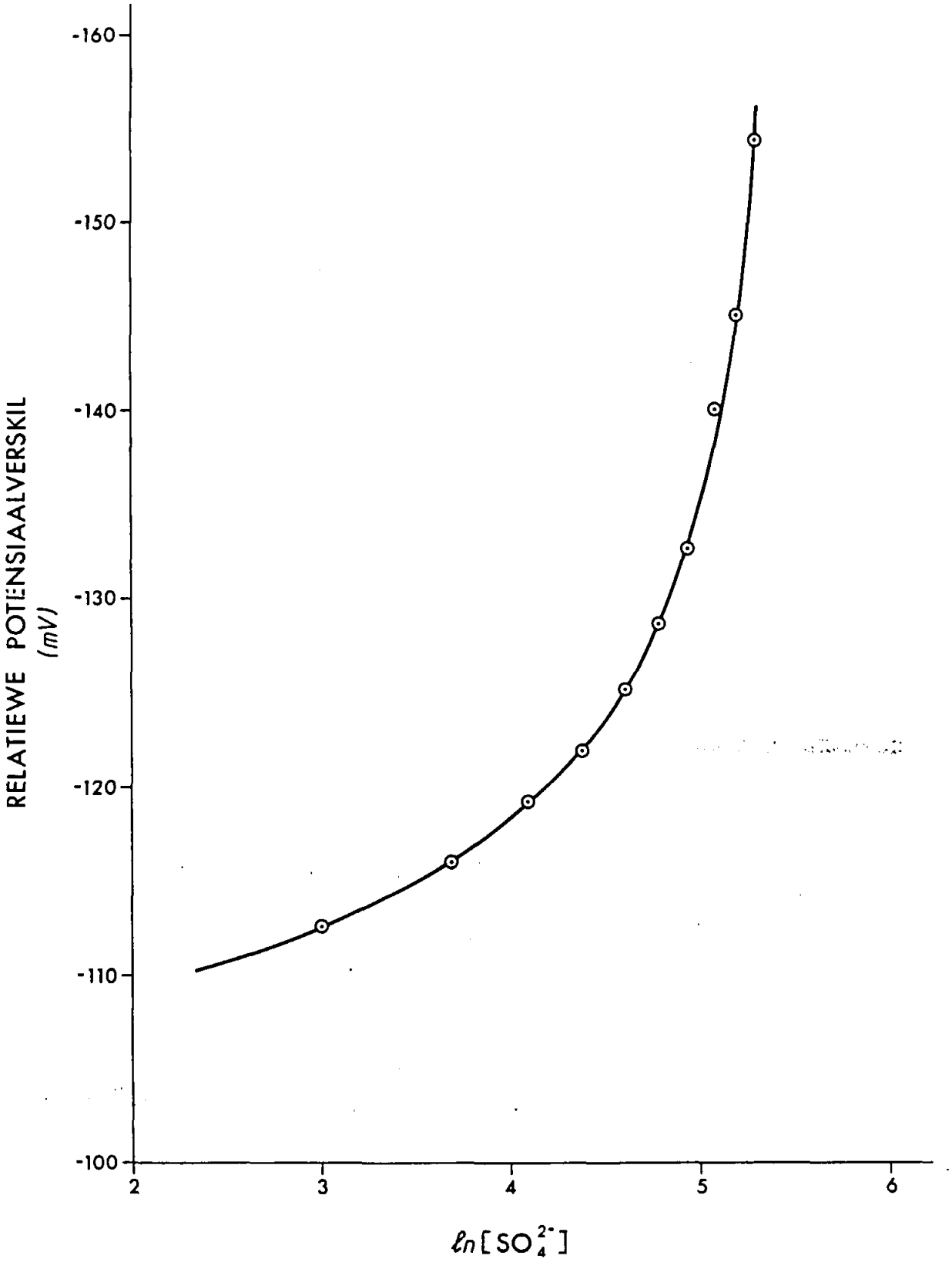
FIGUUR 1:

Kalibrasiekurwes vir 'n aantal water-organiese oplosmiddelmengsels. 25 persent organiese oplosmiddel is elke keer gebruik.



FIGUUR 2:

Invloed van die oormaat Pb^{2+}-ioonkonsentrasie op die vorm van die kalibrasiekurwe.



FIGUUR 3:

Kalibrasiekurwe vir 'n reeks standaard sulfaat oplossings.

The Development of Procedures for Design and Evaluation of Irrigation Systems

Murray Biesenbach
and Badenhorst Inc

WRC Report No. 116/1/87

WATER RESEARCH COMMISSION

THE DEVELOPMENT OF PROCEDURES FOR DESIGN AND EVALUATION OF IRRIGATION SYSTEMS

UMBRELLA REPORT

MURRAY BIESENBACH AND BADENHORST INC
CONSULTING ENGINEERS AND ARCHITECTS
Reg No. 77/04283/21

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1987

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PREFACE

The work presented in this report relates to research, funded by the Water Research Commission, into the development of computer based procedures for the selection and design of irrigation systems. The work has been limited to *pressurized* irrigation, excluding centre pivot and other mechanical move type systems.

The reports on this research have been compiled into three documents, *viz :*

The **Technical Report,** which amalgamates into one document the work presented previously in three annual progress reports for 1982/83, 1983/84 and 1984/85 respectively, as well as the work carried out over the past year (1985/86). The technical report consists of nine chapters, containing detailed presentations of the following :

* Rationale and basic philosophy underlying the research;
* State of the art reviews;
* Analyses of the newly developed algorithms;
* Program flow charts and selected listings;
* Reporting of results of applications of the computer programs.

The **Umbrella Report,** which provides the background to the work carried out over the past four years, as well as a **guide** to the more detailed analyses presented in the technical report. It is intended to give perspective on the routes followed during the course of the research (within the framework of the original commission) and the extent to which the original objectives of the project have been fulfilled. This document is presented in three sections, *viz:*

* **Background to the Project Development.** A brief discussion of the historical development of the project, starting from the original proposal and going through the yearly work programmes;
* **Summary of the Technical Report.** A chapter by chapter summary of the Technical Report;
* **Conclusions.** A summary of the research results and discussion on some directions for future research.

The **Executive Summary,** which is a brief document prepared principally for presentation to the Commissioners of the Water Research Commission. It has been drawn up in the form of a synopsis of the Umbrella Report.

The personnel involved in the research over the past four years have been :

In South Africa (MBB) : J.K Murray, M.A. Todes, J.W Badenhorst and B. Whittall.

In Israel (Karper Engineering) : D. Karmeli, G.Peri, E.Sabbagh and E. Erez.

Computer programming for the block design model was done in conjuction with F. Korb in Pretoria.

Writing of the reports was done by M.A. Todes

The Evaluation Committee responsible for this project consisted of the following members:

Mr D S van der Merwe (WRC) (Chairman)

Mr J K Murray (MBB) (Vice- chairman)

Mr C T Crosby (Directorate of Agricultural Engineering and Water Supply)

Mr F J C Hugo (- do -)

Mr D J du Rand (- do -)

Mr F B Reinders (- do -)

Mr A A Louw (- do -)

Dr A J van der Merwe (Soil and Irrigation Research Institute)

Dr G C Green (WRC)

Mr D J van Rensburg (MBB)

Mr P F Pretorius (Department of Water Affairs)

Dr P C M Reid (- do -)

Mr F P Marais (WRC) (Committee Secretary)

The researchers would like to express their gratitude to the WRC for its support ; and also to the members of the Evaluation Committe for their input during the course of the work.

Murray, Biesenbach and Badenhorst Inc

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CONTENTS

1. BACKGROUND TO THE PROJECT DEVELOPMENT

1.1 Motivation

A research proposal for "The Development of Procedures for the Selection of Appropriate Irrigation Methods and for the Design of Irrigation Systems" was submitted by Messrs Murray, Biesenbach and Badenhorst Inc. (MBB), in association with Karper Engineering, to the Water Research Commission (WRC) in August 1981.

The principal objectives of the proposed research were listed as being :

> "...to develop a **comprehensive procedure for the selection and design of irrigation systems**, such that :
>
> (a) The selected methodology will be the most appropriate in terms of efficient use of water, energy, labour and other relevant economic factors.
>
> (b) The design will consider all system parameters (pump characteristics, local headlosses, flow-pressure relations at each outlet, etc.), and will therefore be accurate.
>
> (c) The expected irrigation performance of a given design will be related to the system and its operating conditions, so that the design can be evaluated, in order to enable the selection of optimal systems."

It was proposed that these objectives could be realized through the development of **computer based irrigation design models** and that the research would therefore concentrate on the development of these models. More specifically, the models would be structured to provide the designer with a series of parameters that enabled an evaluation of the designed system.

It was proposed furthermore that these parameters could be used to generate some general cost versus performance relationships which could be incorporated into normal design practice. For this purpose it was proposed that the research effort would include an analysis of a number of South African farms, using the design models.

Discussion held during the clearance meeting for consideration of the proposal (October 1981), centered around two main issues. Firstly it was considered important that **the design models should be practically applicable at a farm level**, rather than being purely theoretical. Secondly, the need to incorporate a thorough, **economically based, cost/benefit evaluation of the designed systems** was stressed. Accordingly, these two issues were incorporated as specific objectives of the research.

A budget for a three year research project was approved in March 1982, and work commenced in June of that year.

MBB entered into an agreement with Professor D. Karmeli of Karper Engineering Ltd. (Israel) to carry out the work on a joint project basis. Professor Karmeli was appointed as Principal Researcher, and under his direction, two separate research teams were appointed. The first, which consisted of engineers from Karper based in Israel, worked on the theoretical aspects related to the model development. The second team of engineers from MBB, based in South Africa, worked on the field-based data collection.

1.2 First Year

The work during the first year of the research was divided into six specific tasks as follows :

Task 1 : Classification of irrigation practice in South Africa on a regional basis, for the purpose of identifying the most suitable areas for an in depth survey of selected farms (task 2). A brief report on this work was compiled and the work was then extended into a review and analysis of the state of the art in the development of crop water-yield relationships. These relationships were seen as being the key to the economic evaluation of the designed systems.

Task 2 : In depth surveys of the irrigation systems operating on a number of selected farms, with the aim of using the information from these surveys to test the design models once they were operational.

Difficulties were experienced with this aspect of the work on two counts : firstly, original design data on the operating systems was difficult to come by and in many instances was incomplete. Secondly, this work was carried out simultaneously with the work in tasks 3 and 4, which concentrated on the development of the design models. Thus at that stage the exact requirements of the design models were not fully defined and it was difficult to establish

the precise needs from the surveys. This problem was exacerbated by the fact that the design models were being developed by a team working in Israel, whilst the surveys were being carried out in South Africa.

Task 3 : A review of the state of the art of current design practices, aimed at identifying the specific shortcomings of current practice, and developing approaches for the development of the proposed computer based design models. This work resulted in a classification of the design process into three distinct modules, namely preliminary design, block design and mainline design. For each of these modules a set of specific design parameters was formulated.

Task 4 : This task concentrated on the mathematical formulation of the algorithms to be incorporated into the proposed computer based design procedure. Separate models were formulated for each aspect of the design process, as identified in task 3.

Task 5 : A review of the state of the art in the evaluation of irrigation systems. Most of the work in this subject relates to the evaluation of systems already in operation in the field. However it was felt that this work could provide a basis for the required evaluation model.

Task 6 : Extension of the work in task 5 to the formulation of an evaluation model, to be incorporated into the computerized procedures. A model was proposed for the overall evaluation of a completely designed system. It incorporated an assessment of the expected yield that would result from the designed system and a dynamic programming routine to optimize the operating regime for the designed system.

1.3 Second Year

The work during the second year concentrated principally on utilizing the work done in the first year, in tasks 3 to 6, to develop the proposed computer models. The programs were written in PASCAL for the HEWLETT PACKARD 9816 computer. Three specific sets of programs were developed, as follows :

Preliminary Design/Emitter Selection : The computer programs for preliminary design incorporated : a data base containing information on the operating characteristics of emitters, to be used in the selection of an emitter; a program to calculate the basic agronomic parameters regulating the preliminary design process; and a program to incorporate the

agronomic parameters with the information in the emitter data base in order to generate a list of feasible emitters for a given design.

Block Design : The block design process involves determination of the diameters of the in-field pipe network, together with their operating hydraulic characteristics. The computer models that were developed during this phase of the work utilized poly-plot type algorithms for determination of the pipe diameters, and incorporated a block evaluation program. This latter program provided an assessment of the various economic factors related to the block design.

Mainline Design : The computer programs developed for mainline design incorporated a linear programming algorithm for optimization of the trade off between capital and operating costs.

1.4 Third Year

The third year of the research entailed using the design models to design systems for the farms surveyed as part of task 2, described above. These designs were then to be compared with the existing designs on these farms, in order to derive conclusions about both the effectiveness of the new design procedures and the prevailing cost versus performance relationships for South African conditions.

1.5 Fourth Year

At the end of each year of the research, a comprehensive report on the work carried out during the preceding year was presented. At the end of the third year, a Subcommittee of the Project Evaluation Committee was convened by the WRC, with a brief to consider the three annual reports, prior to their final acceptance at a concluding meeting of the Evaluation Committee. This Subcommittee called for comments on the three progress reports from various people involved in the research and a set of documents was issued six months after the end of the third year, summarizing these comments.

In general, it was felt that :

* the models did not provide the type of economic evaluation that had been specified as part of the objectives of the project;
* the three progress reports did not satisfy the WRC's requirements for final project reporting; and that a single document synthesizing the work covered in the progress reports should be produced.

In addition, some conceptual errors in the design algorithms and arithmetic errors in the evaluation algorithms were identified.

In order to enable MBB to attend to these comments, the WRC extended the project by a further six months. Initially, the work involved trying to utilize the computer programs that had been developed by Karper in Israel during the first three years of the research. The computer models had to be modified in order to rectify the errors that had been identified previously and to provide the required evaluation capabilities. However, this proved to be difficult and it was decided that it would be easier to redevelop the programs.

Two new sets of programs were developed. The first, written in BASIC for the IBM PC, covered mainline design; and the second, written in PASCAL also for the IBM PC, covered the block design problem. In developing these programs, the work concentrated firstly on making the evaluation algorithms as comprehensive as possible and secondly on making the computer programs as "user friendly" and flexible as possible; thereby addressing the objectives of the project as summarized above.

2. SUMMARY OF THE TECHNICAL REPORT

The technical report is divided into three parts as follows :

* **Part 1 : Basic Theory.** This section deals with the motivation for the research, and covers the theory that forms the basis of the research work.

* **Part 2 : The Models.** This section gives a full analytical description of the design models that have been developed.

* **Part 3 : Results.** This section describes some applications of the models, and summarizes the conclusions that have emerged from the work.

Within each of these sections, the individual chapters are as follows :

Part 1 : Basic Theory

Chapter 1 : Rationale
This chapter covers the motivation for the project.

Chapter 2 : Systems Analysis of the Design Process
This chapter provides an analysis of the irrigation design problem, identifying each different aspect of the process and the respective design parameters.

Chapter 3 : Review of Irrigation Quality Analysis
A review of the state of the art of evaluation of irrigation systems, leading to proposals for the computer model.

Part 2 : The Models

Chapter 4 : Block Design
Details of the block design model, and the associated computer programs.

Chapter 5 : Evaluation of the Block Design
Details of the evaluation model that forms part of the block design process.

Chapter 6 : Mainline Design

Details of the mainline design model and computer programs.

Part 3 : Results

Chapter 7 : Applications of the Block Design Programs

Description of some applications using the models.

Chapter 8 : Applications of the Mainline Design Programs

Description of some applications using the models.

A summary of each of these chapters is presented in the following pages.

2.1 Chapter 1 : Rationale

This chapter presents a basic motivation for the research project. Two specific topics are discussed. The first concerns the irrigation design problem itself and the aims of the work in terms of improving current approaches to irrigation design. The second topic is the impact of recently developed computer aided design technologies in engineering design. Discussion is given on the potential advantages of incorporating these technologies into the irrigation system design process.

A brief review of the irrigation design process is given, in which the design problem is related to the determination of two sets of characteristics, namely hardware and system characteristics. The hardware characteristics include the physical attributes of an irrigation system, such as the type and size of the emitters, the pipes and the accessories (valves, fittings and pumps). The system characteristics include the non-physical attributes of a system, such as the system capacity, the operating regime, the layout of the pipes and the system performance.

A generalized design process consisting of five distinct steps is outlined. These steps are respectively :

a) Establishing the operating constraints.
b) Selecting an emitter and thereby establishing the actual operating regime.
c) Block design.
d) Mainline design.
e) Establishing the pumping and control systems.

From a description of these five steps, the basic criteria currently used for the design of irrigation systems are identified as :

* An operating regime defined by pre-determined soil, plant and field-geometry characteristics.

* Uniformity of application defined by adherence to the 20% rule (maximum variation of pressure in a given block limited to 20%).

* Minimum system and operating costs.

* Maximum yield.

A number of shortcomings of current approaches to irrigation design are then discussed. These include :

* The use of the minimum cost/maximum yield criteria rather than a maximum profit approach. In this regard, the potential for so called "deficit irrigation", or deliberate under-irrigation in order to achieve higher returns on investment, is discussed.

* The need to rationalize the final design in terms of a well defined set of objectives.

* The need to measure the expected performance of the final design on the basis of a set of explicit parameters, rather than on the basis of the 20% rule, which is a surrogate measure.

* The need to identify and understand the implications of the various trade-offs involved in the design process, such as cost versus performance, system versus operating costs, block network versus mainline network and flexibility of operation.

The research attempts to address these shortcomings in the formulation of the models.

Finally, the development of computer aided design (CAD) technologies in the engineering design process is discussed. The different types of systems are described, and the fact that these systems do not provide an "A to Z push button" solution to the design process is stressed. Rather, they provide the engineer with a tool to investigate aspects of the specific design problem that could not practically be considered previously. The research aims to incorporate the full potential of CAD technology into the development of the design models.

In summary the aims of the research are given as :

* The carrying out of a comprehensive systems analysis of the design process.

* The formulation of measurable performance and quality of irrigation related design criteria, for use in the design process.

* The development of a suite of programs for computer based design of irrigation systems, utilizing the full potential of CAD technologies.

* Formulation of cost versus performance relationships based on a sensitivity analysis of the various design parameters.

2.2 Chapter 2 : Systems Analysis of the Design Process

This chapter aims to provide a systematic analysis of the whole process involved in the design of irrigation systems. This is done for the purpose of structuring and then developing the computer based design models. The analysis is carried out in four parts, as follows :

* Firstly, the requirements of the design process are examined, leading to an identification of the individual components of an irrigation system that have to be designed.

* The second step is to identify the phases involved in the design process. In other words, to assign the design of the numerous components identified in the first step described above, to a series of distinct design phases and thereby build up a structure for the design process.

* The third step involves more detailed analysis of each of the design phases, in order to identify the specific design problems associated with each of these phases. This entails identifying : the input requirements for each phase; the individual design steps contained within each phase; the general design routines and constraining factors related to each of these design steps; and finally, the output from each phase.

* The last part of the systems analysis looks at the principles involved in the structuring and design of the actual computer programs.

In the first part of the analysis, the components that have to be designed are classified into two groups, as mentioned in the review of Chapter 1 above. These are, respectively, hardware and system characteristics. Table 2.1 shows a list of the components contained in each of these groups. The actual design requirements in each case are listed under the component, and the right hand column shows the design parameters which affect the design of each component.

From this classification, a structure for the complete design process has been developed, as shown in figure 2.1. It can be seen from the figure that the basic process consists of three distinct phases, namely input, design and output. Within the design phase, a further three sub-phases or "modules" have been identified. These are respectively :

Table 2.1 System components and associated design parameters

	Component	Design Parameters
	Hardware	
I.	Emitters - type	Spacing; Nominal operating pressure; Costs; Pressure/discharge relationship; Operating regime;
ii.	Block network - lateral pipe diameters - manifold diameters	Hydraulic grade line; Allowable pressure variation; Coefficient of uniformity; Pipe alignments; Topography; Pipe costs;
iii.	Mainline network - pipe diameters	Hydraulic grade line; Pipe costs; Energy costs; Flow and pressure requirements;
iv.	Control elements - valves : type, size; - flow and pressure regulators : if needed, type, size - meters : if needed, type, size - automation equipment : if needed, type - filters : if needed, type, size	Flow and pressure requirements; Hydraulic grade line; Discharge volumes; Water quality; Costs;
v.	Pumps - main pump size - booster pump sizes - fertilizer injection equipment : if needed, type, size	Hydraulic grade line; Discharge volumes; Flow and pressure requirements; Costs;
	System characteristics	
I.	Capacity - maximum system discharge - flow and pressure distribution - system application rate - maximum application depth	Pump size; Pipe sizes; Emitter discharge; Max. block size; Emitter pressure; Emitter spacings; Irrigation set time;
ii.	Layout and alignments - division of field into blocks - emitter spacings - orientation of laterals - positioning of manifold - location of block valves - configuration of mainline network	Operating regime; System application rate; Pressure and flow requirements of emitters; Maximum length of a single or double diameter pipe; Topography; Pressure and flow requirements of valves;
iii.	Control system - location of control elements - degree of automation	
iv.	Operating regime - irrigation set time - irrigation cycle length - timing of irrigation sets (i.e. times of the day, days of the week) - sequencing of block valves - filter flushing programme - fertilizer injection programme	Readily available soil moisture; Peak daily irrigation requirement; Number of irrigation blocks; System capacity; System application rate; Degree of automation;
v.	Pumping requirements - maximum pumping capabilities - the pumping regime, including operation of booster pumps	System capacity; Operating regime; Hydraulic grade line; Flow requirements;
vi.	Performance - coefficient of uniformity - application and requirement efficiencies - capital and operating costs - return on investment	All design components

* **Preliminary design;**
* **Block design;** and
* **Mainline design.**

Figure 2.1 illustrates the fact that the design process does not involve starting at a particular point and working steadily through a number of routines until the design is complete. The inter-relations between the various components are complex, and the design process therefore involves continuous iteration, both within and between each module.

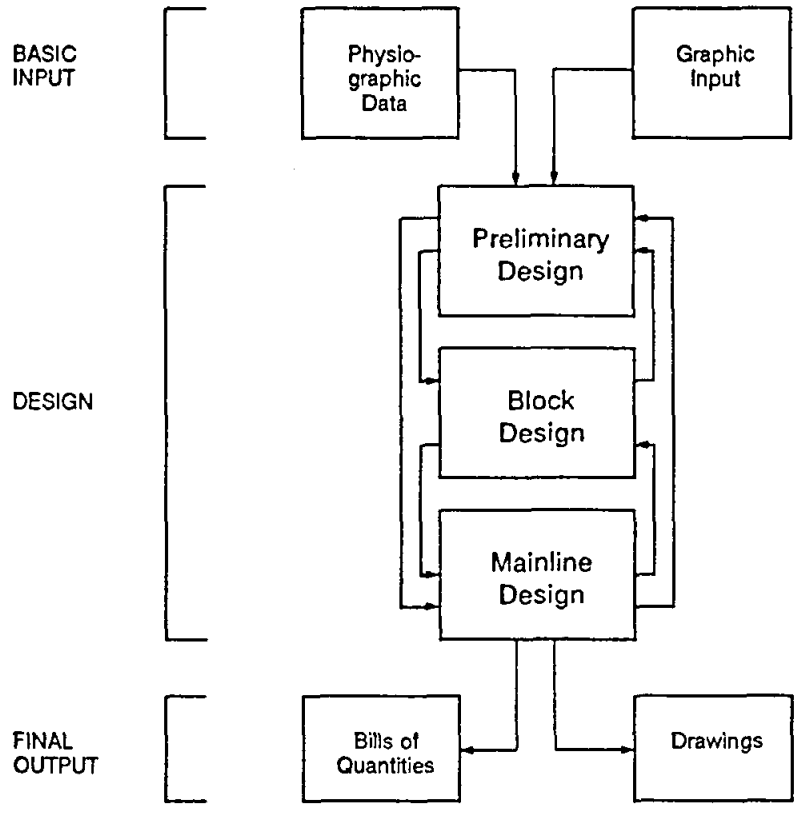


Figure 2.1 : Phases in the Design Process

Figure 2.2 shows the individual design steps in each of the three modules, together with the input requirements and the output from each of these steps. An analysis of the specific design problem related to each step is given in the technical report.

The design and structuring of the computer programs is considered to be an important aspect of the research, since their utility as a design tool is directly affected by their efficiency of use and their accuracy. The more flexible they are, the greater the extent to which the

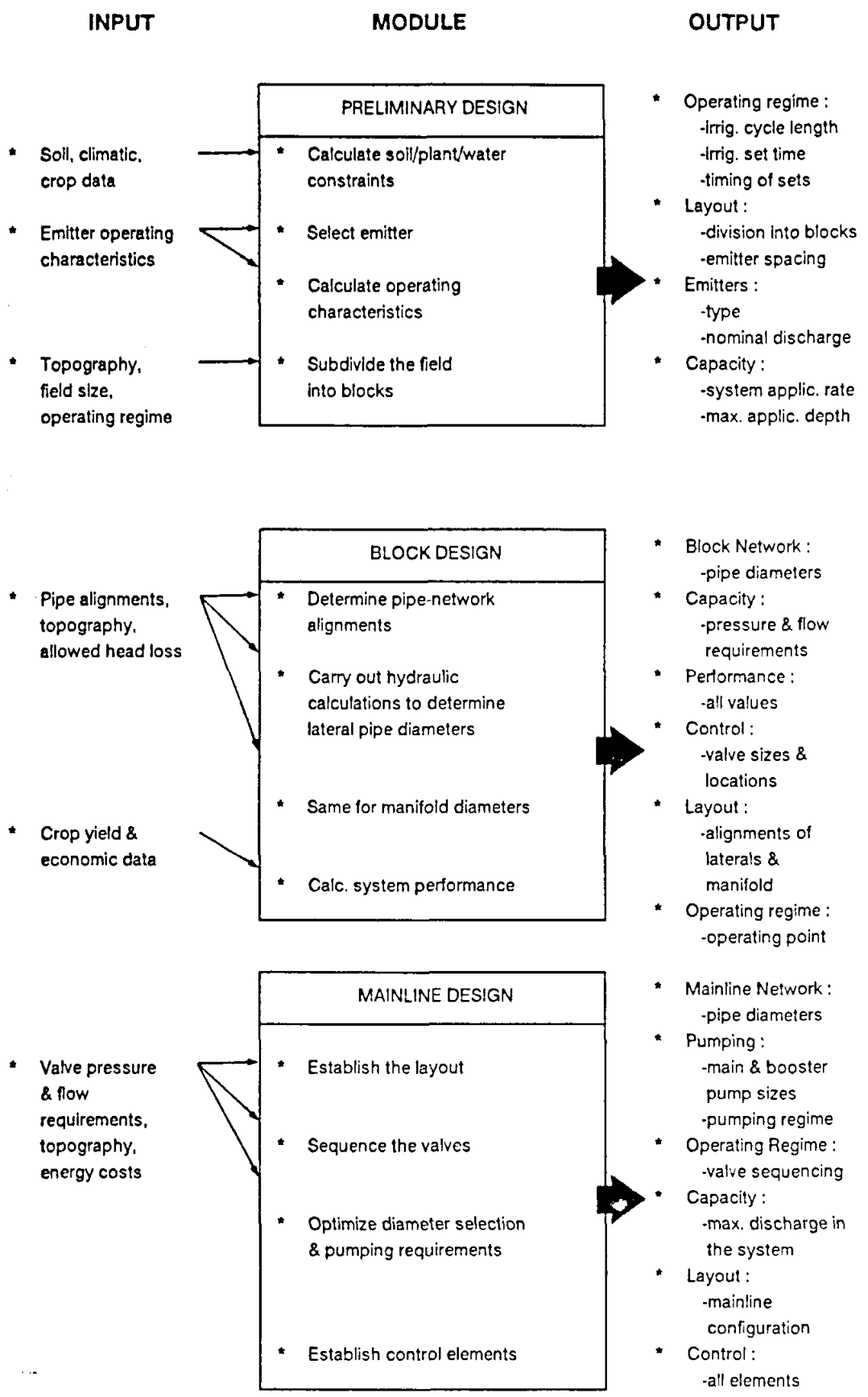


Figure 2.2 : The Design Modules

designer can explore different design considerations. Good software design relates to three aspects of a program's operation. These are firstly the actual analysis routines, secondly the the process of validation of input data prior to executing the various analyses and thirdly the nature of the man-machine interface.

The program is operated via an interactive dialogue with the designer. The purpose of this dialogue is to assist the user in inputting the required data and then to guide him through the design process. In this latter regard the interaction should not be an inflexible step by step process, whereby the user's role is a passive one of merely inputting the data and then reading the results of the analysis. Since ultimately all design decisions should be made by the designer, the interactive procedure should ensure that the user receives full information regarding all options in a multi-objective problem, and in such a form that he is able to make a correct and well informed decision.

2.3 Chapter 3 : Review of Irrigation Quality Analysis

This chapter consists of a review and analysis of the literature related to the evaluation of irrigation systems, for the purpose of formulating an evaluation model as part of the design procedure. Most of the reported work relates to the evaluation of irrigation systems operating in the field. Such evaluation generally entails measuring the quantities of water released by the system throughout the field. On the basis of these measurements a number of different statistics can be derived, which characterize the quality of the irrigation.

These statistics can be classified into two groups as follows :

* **Efficiency,** which measures the extent to which the water drawn into the irrigation system is usefully used.

* **Distribution Uniformity,** which measures the extent to which the quantity of water applied during an irrigation varies throughout the field.

A large number of different efficiency and uniformity measures have been proposed in the literature, and these are all reviewed in the technical report. An analysis of all of these statistics shows that a combination of two of the efficiency measures and one of the uniformities provides an adequate picture of the irrigation quality, and that in fact all of the other measures can be equivalenced to these three statistics. They are, respectively :

* **Water Application Efficiency,** which is the fraction of the total irrigation application that is made available to the plant, rather than being lost to evaporation and deep percolation.

* **Water Requirement Efficiency,** which is the fraction of the plant water requirement at the time of irrigation that is met by the irrigation.

* **Christiansen Uniformity Coefficient (UCC),** which is given by :

$$UCC = 100\,[1 - (\sum_{i=1}^{N} |X_i - \bar{X}|) / N\bar{X}] \qquad (1)$$

Where N = the number of observations X_i

$\bar{X}$ = the average application depth.

These three measures are therefore incorporated into the evaluation model, as discussed in Chapter 5. In order to extend this analysis further, to include measures of the economic cost/benefit ratios resulting from a designed system, it is necessary to be able to estimate the crop yield that will result from the use of the irrigation system. This in turn requires the use of the so called *yield/water* functions that have been formulated in the literature. Crop yield has been found to be dependent on numerous factors and it is difficult to isolate the crop response to water on any consistent basis. Nevertheless, some empirically based relationships have been proposed in the literature, and these can be used for the required analysis.

The total yield, Y, expected from a field of area A_t is given by the integral :

$$Y = \int A_t \, y(i) \, f(i) \, di \qquad (2)$$

Where $y(i)$ = the yield per unit area achieved as a function of the irrigation depth i.
$f(i)$ = the frequency distribution function of irrigation depths, for a given irrigation.

Then, given the total yield, Y, a profit maximizing objective function can be expressed by :

$$\text{Max[NE]} = Y(P_y - K_y) - V_a C_w \qquad (3)$$

Where **NE** = the net earnings achieved through irrigation.
P_y = the price earned per unit of yield.
K_y = total production costs per unit of yield.
V_a = the total volume of water applied in the field.
C_w = the irrigation system capital and operating costs, rationalized over the expected life of the system and expressed in terms cost per unit of water.

The constraints required to formulate the full optimization problem consist of the complex set of functions determining the cost C_w and the volume V_a, together with the integral in equation 2. One of the most significant problems related to the above models is the obtaining of sufficiently accurate yield/water functions. It is believed however, that with the on-going research and development of these relationships, various adaptations of the models will increasingly be incorporated into the design process. One such adaptation is proposed in Chapter 5 of the Technical Report.

2.4 Chapter 4 : Block Design

The main elements of the block design problem are :

* determination of the pipe alignments;
* determination of the pipe sizes;
* evaluation of the system performance resulting from the designed system.

2.4.1 Pipe alignments

These are normally established largely on the basis of the designer's intuition. The lateral pipes are aligned parallel to the planted rows; and the manifold then transects the laterals. The position of the manifold is determined on the basis of both practical convenience and hydraulic considerations.

Practical convenience is dictated by factors such as accessibility to pipes in the field and the position of existing elements. The hydraulic considerations arise out of the fact that the manifold may divide the laterals into two sets, lying on either side of the manifold. Ideally, the manifold should be positioned such that the lengths of the laterals running uphill away from the manifold are maximized, within the constraints of the allowable pressure loss in the system.

2.4.2 Pipe diameters

The pipe diameters are established using the allowed pressure variation in the system as a design parameter. The general procedure for a given pipe involves first of all establishing a pressure envelope, defined by the topographic elevations along the length of the pipe and the allowable pressure variation within the pipe. The upper and lower limits of the envelope represent the maximum and minimum allowable *hydraulic grade lines* respectively, along the pipe being designed. Then, starting at the furthest end of the pipe with the smallest available diameter, the pressure head in the pipe is calculated for points along its length, working back towards its inlet. This pressure head will increase exponentially as the flow in the pipe increases because more and more outlets are included along the length being considered. Considering this curve in the other direction (i.e. in the direction of flow in the pipe), the exponential shape represents the decreasing rate of head loss due to friction, per unit length, as the flow in the pipe decreases. As soon as the **actual** hydraulic grade line for the diameter of pipe being considered starts to rise steeply towards the upper limit of the allowed envelope, the pipe is replaced by a larger diameter, thereby reducing the rate of pressure loss due to friction. The process then continues until the inlet is reached. In this way a set of diameters and their respective lengths are determined, such that the pressure variation in the lateral is contained within the allowable limits.

Several algorithms for carrying out this design process and simultaneously obtaining a least-cost design have been proposed in the literature. They are reviewed in the technical report. The model developed as part of the research program is based on the widely used "poly-plot" graphical process, as formalised for computer applications by Professor Perold at the University of Stellenbosch (see the technical report for full references). A feature of the model is that it incorporates accurate calculations of the emitter flow/pressure relationship, rather than assuming a constant discharge along the length of the pipe.

The full block design process entails carrying out the diameter design for each lateral in turn, and then using the results from the lateral design in a similar procedure for the manifold. At the end of this process, the pressure and flow required at the block valve, for irrigation of the block, are known.

2.4.3 The computer models

The computer models for block design have been integrated into a single package, as shown in the synoptic map in Appendix 1. The package is menu driven and consists of three principal modules : the **layout module**, the **design module** and the **evaluation module.**

Layout entails specifying details of the system alignments such as :

* the emitter and lateral spacings;
* the lengths of the laterals and the manifold; and
* the elevations of the pipes.

Once this has been done, then the actual pipe design can be carried out.

The pipe diameters for individual laterals can be designed using the algorithm described above. Output from this procedure includes :

* a display of the pipe flow and pressure characteristics;
* a graphical plot of the allowed pressure envelope and the pipe hydraulic grade-line (see figure 4.1); and
* a summary table of the operations performed in the design proces.

Alternatively a series of laterals can be designed by proportional extrapolation of results previously obtained for two other laterals that have already been designed. This facility enables the designer to ensure that the positions of any pipe changes lie along a straight line in a field. This greatly facilitates the installation of the system.

Once a lateral has been designed by the computer, the designer may alter the design manually by editing a displayed table of the design results, as shown in figure 4.2. As can be

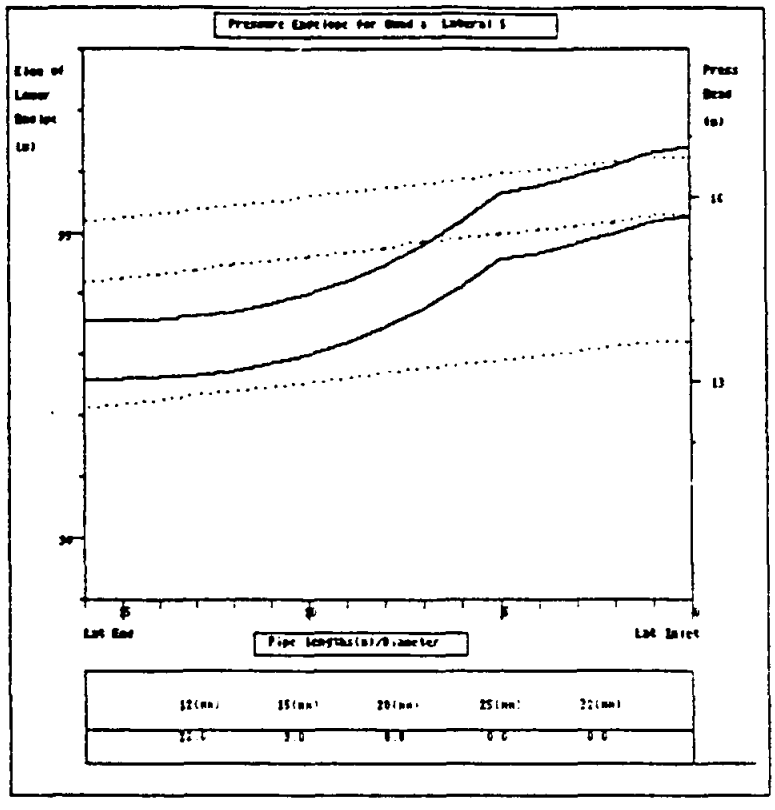
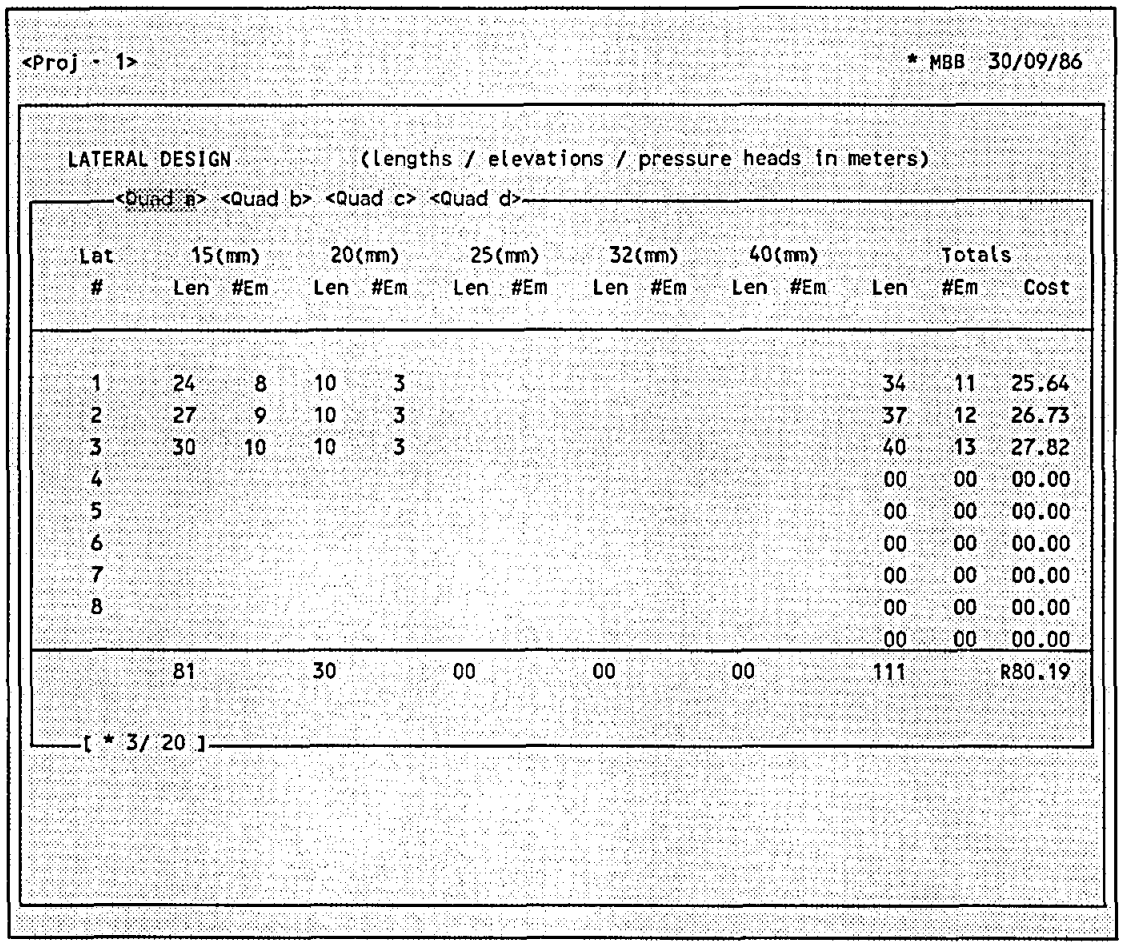


Figure 4.1 : Graphical plot of the pressure profile resulting from the lateral design process

seen in this figure, the designer has a continuously updated display of the cost of each lateral, the total cost of all designed laterals and the total lengths of each pipe diameter used. Thus the effects of any changes can be monitored by the designer.

In addition to the three principal modules, a series of **"pop-up" utilities** have been developed as an aid to the operator. These utilities can be evoked at any stage during operation of the main program by pressing the relevant function key on the computer keyboard. They operate by popping up a separate window, over the current display on the computer screen, without altering whatever is currently displayed.



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LATERAL DESIGN (lengths / elevations / pressure heads in meters)

<Quad a> <Quad b> <Quad c> <Quad d>

Lat #	15(mm) Len	#Em	20(mm) Len	#Em	25(mm) Len	#Em	32(mm) Len	#Em	40(mm) Len	#Em	Totals Len	#Em	Cost
1	24	8	10	3							34	11	25.64
2	27	9	10	3							37	12	26.73
3	30	10	10	3							40	13	27.82
4											00	00	00.00
5											00	00	00.00
6											00	00	00.00
7											00	00	00.00
8											00	00	00.00
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[* 3/ 20]

Figure 4.2 : Table of results of the lateral design process

The utilities provided are respectively :

* A **maximum length calculator,** which enables a rapid calculation of the maximum lengths of pipe for two diameters, that can be used for a given emitter operating on a given slope at a predefined nominal pressure and with a predefined allowable pressure loss. This facility is useful for determining the optimal positioning of the manifold.

* paging through and updating both the **pipe and emitter databases.** These databases provide all relevant information on available equipment, such as costs, sizes and in the case of the emitters, performance characteristics.

Figure 4.3 illustrates the computer screen during simultaneous operation of the maximum length calculator and the emitter database. The designer can page through the available emitters to find the required one and then transfer it across to the maximun length calculator.

The block design programs also include the evaluation models, which are discussed in Chapter 5.

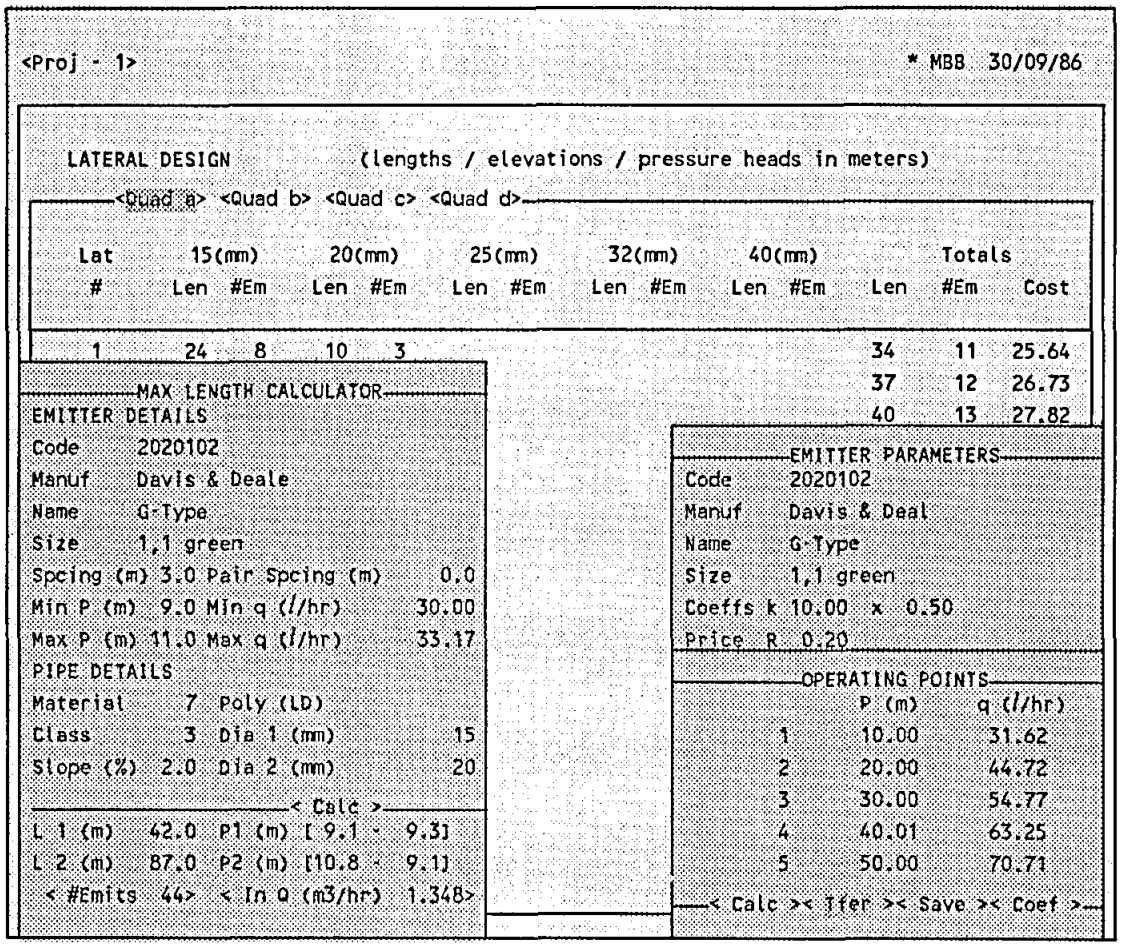


Figure 4.3 : The maximum length calculator and emitter database "pop-up"

2.5 Chapter 5 : Evaluation

This chapter extends the work reviewed in Chapter 3, leading to the formulation of an evaluation model that forms part of the block design process. The chapter is presented in five sections as follows :

2.5.1 Basic Model Structure

The proposed model contains two distinct evaluation phases. The first looks at the *water distribution uniformity* that will result from the designed system and the second involves the *economic cost/benefit analysis*. An outline of the basic input and output in each of these analyses is shown in figure 5.1.

The water distribution pattern resulting from the designed system will in fact vary depending on the pressure at the inlet to the block. For this reason the evaluation is carried out for four different inlet pressures, thereby enabling the designer to develop a feeling for the sensitivity of the overall system performance to this parameter. The particular parameters that are considered in this analysis are listed under the "OUTPUT" column in figure 5.1.

Using these parameters, the designer is able first of all to assess the overall performance of the designed system in terms of its distribution functions, and secondly to establish the optimal inlet pressure at which to operate the system.

The second evaluation analysis entails estimating the yield that will result from the designed system and then comparing the income resulting from the yield with the various costs involved in generating this yield. The evaluation is carried out on the basis of the economic return, both per unit area and per unit of water used. The specific parameters generated by this analysis are shown in figure 5.1.

The main measure of *financial return*, generated by the analysis, is the **equivalent annual worth (EAW)**, which is established as follows : the Net Present Worth (NPW) of the system is calculated using diferent inflation rates for *energy costs*, other *production costs* and *producer prices* respectively. The EAW is then the NPW, converted back to an annual figure on the basis of the expected life of the system and the prevailing *general* rates of inflation and interest, which reflect the overall cost of money.

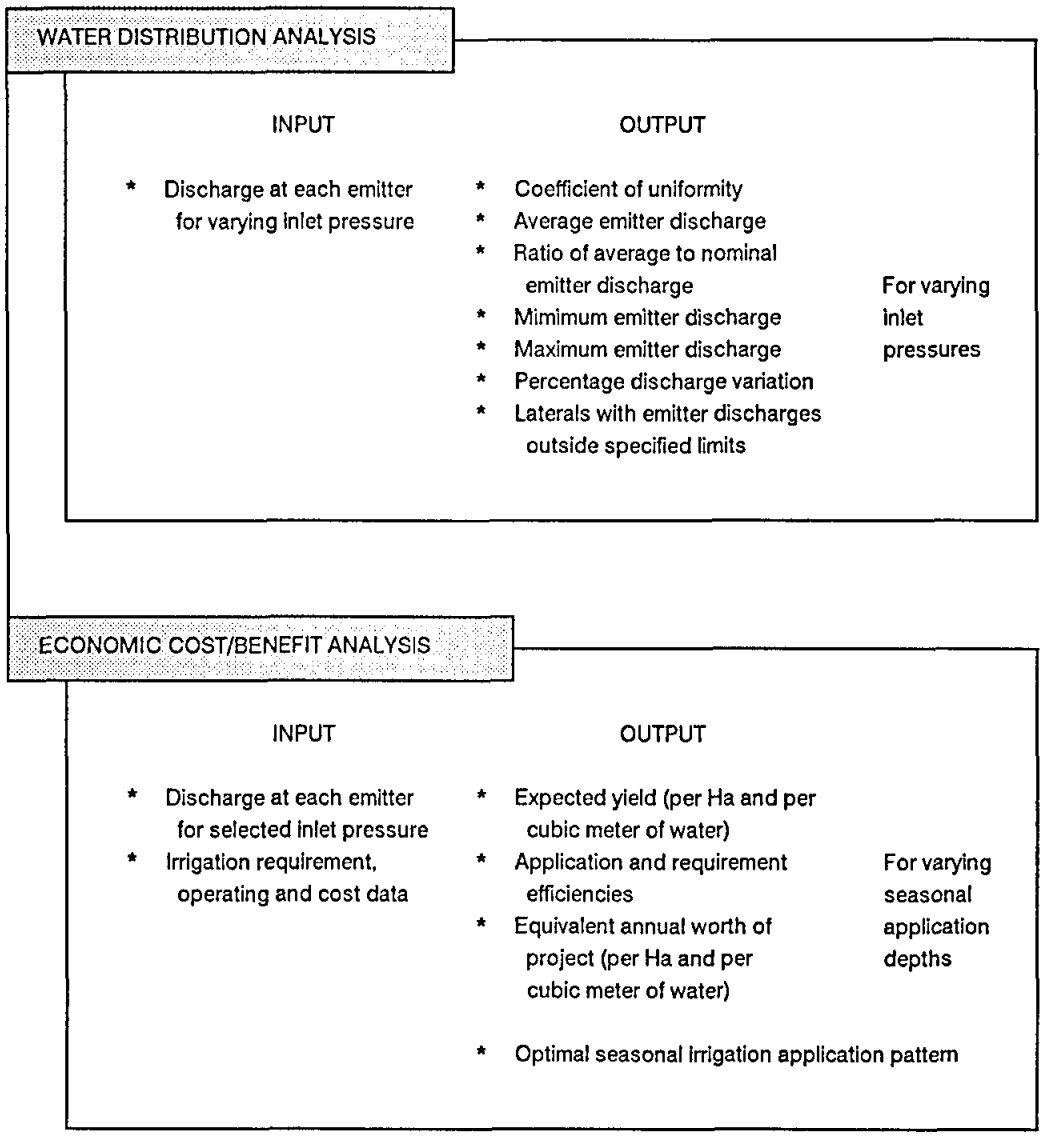


Figure 5.1 : Evaluation Model for Irrigation System Design

2.5.2 Operating Point

All of the parameters that result from the economic evaluation are dependent on the actual seasonal application depth. This depth is a function of the real time operation of the system and can in fact be varied within a range from zero up to the capacity of the system. It is therefore referred to as the "operating point" of the system.

Since a system is normally designed to meet the expected seasonal irrigation requirement at minimum cost, this requirement level should correspond to the capacity of the system. The irrigation requirement is defined as the amount of water required to produce maximum yield. If the system is operated throughout the season at less than its capacity, then the yield may not be maximized, but the *operating* costs will be reduced. There is thus a trade off which may

imply a better economic return from so called **deficit irrigation.** The economic return may be further improved by purposely designing the system for a lower capacity (less than the seasonal requirement), thereby also reducing the *capital* costs.

The evaluation model includes an analysis of this aspect of the design. A dynamic programming algorithm has been developed to determine the optimal seasonal operating point for the designed system, based on the expected requirement in individual periods during the season. The parameters listed above for the economic evaluation are generated for five different operating points and the results plotted on a graph which shows the sensitivity of the system to the operating point.

2.5.3 Yield

The question of the water/yield function is a sensitive one as the issue is not fully resolved in the literature. In practice, any accepted function could be incorporated into the analysis. The model which has been used is the linear one, which is given by :

$$(1 - Y_a/Y_m) = k_y (1 - I_a/ET_m) \quad \text{for } I_a < ET_m$$
$$Y_a = Y_m \quad \text{for } I_a >= ET_m \qquad (4)$$

Where
- Y_a = the actual yield,
- Y_m = the maximum achievable yield,
- I_a = the irrigation application,
- ET_m = the maximum evapotranspiration, and
- k_y = is a factor relating the sensitivity of the specific crop to under-irrigation.

This model is supported by a wide body of literature, which is reviewed in the technical report.

2.5.4 Economic Analyses.

The most appropriate method of cost/benefit analysis to be incorporated into the evaluation model is also a contentious issue, since it is dependent on the objectives of the specific project being designed.

Specific issues that must be considered include :

* **The cost of water.** The basic cost of the water used for irrigation may be charged directly to the user by the supplier, in which case it is quite straight forward to calculate. However, in some cases, the water supply may be subsidized and then the rate to be included in the calculations depends on the purpose of the analysis.

When the available supply of water is limited and a number of alternative uses are being considered, then an *opportunity* cost can be attached to the cost of the water. This represents the potential additional benefits that could be derived from using the water elsewhere. The opportunity cost of water is particularly relevant in the case of deficit irrigation, where reduced application will result in a saving of water.

* The **Interest (discount) rate** employed in the analysis. For normal investments of a private nature, the opportunity cost of the investment represents a reasonable measure for calculating the economic worth of the project. In other words, the discount rate can reasonably be taken as being equal to the prevailing bank rate, which is equivalent to the basic cost of money. However, there is varying opinion with regard to the evaluation of agricultural projects. One school of thought proposes that farmers generally take a long term view of their operations, and that any development cannot be evaluated purely in terms of the immediate return on investment that will be realised from the development. This would mitigate for lower interest rates. However, an opposing approach argues that the discount rate should reflect the high risk involved in all farming operations and should therefore be pitched somewhat higher than prevailing bank rates.

* **Inflation.** Several different methods exist for the incorporation of the effects of inflation into economic analysis. In the case of agricultural projects, the economic forces controlling the various facets of the project result in a number of different prevailing inflation rates. These include the rate of energy cost inflation, the inflation rate relating to production costs, inflation of producer prices and finally the general rate of inflation on the overall cost of money.

The analysis used in the proposed evaluation model uses a direct comparison of earnings versus costs. Apart from the provision for inclusion of the opportunity cost of the water, no attempt is made to formulate monetary values of any *indirect* costs or benefits that may accrue from the project.

2.5.5 The Computer Models

The computer model for evaluation attempts to provide the user with full flexibility to consider all the aspects of the evaluation which have been discussed above. The model operates from six different pages, or "screens", which the user can select at will from the evaluation menu.

The first two pages present the results from the *uniformity* evaluation, as shown in figures 5.2 and 5.3 respectively. The results are shown for four different inlet pressures. The user may input a new inlet pressure, for which the uniformity evaluation will be calculated or, alternatively, he can select the inlet pressure to be used for the *economic* evaluation.

Pages 3, 4, and 5 are used for inputting the required data for the economic evaluation and page 6 represents the results of this evaluation, as shown in figure 5.4.

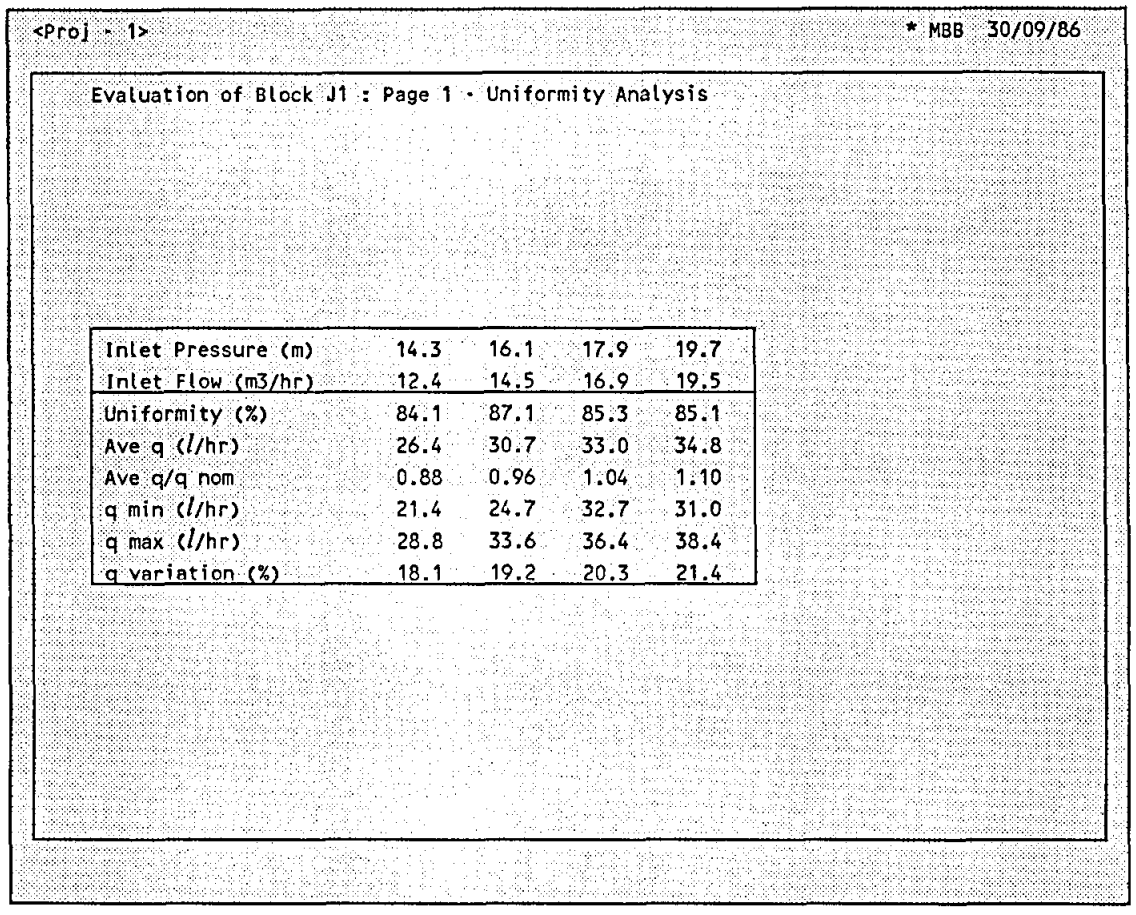


Figure 5.2 : Results from the uniformity analysis of the block evaluation model

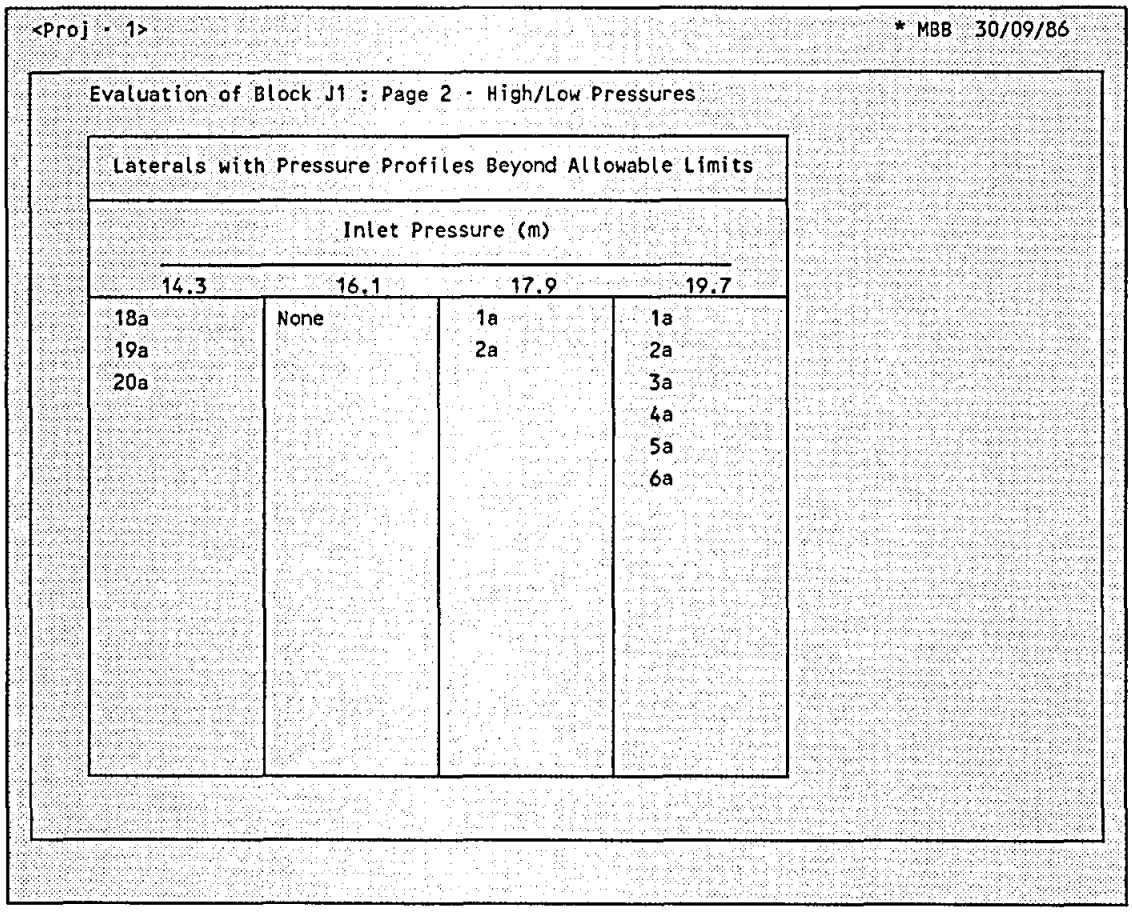


Figure 5.3 : Results from the uniformity analysis of the block evaluation model

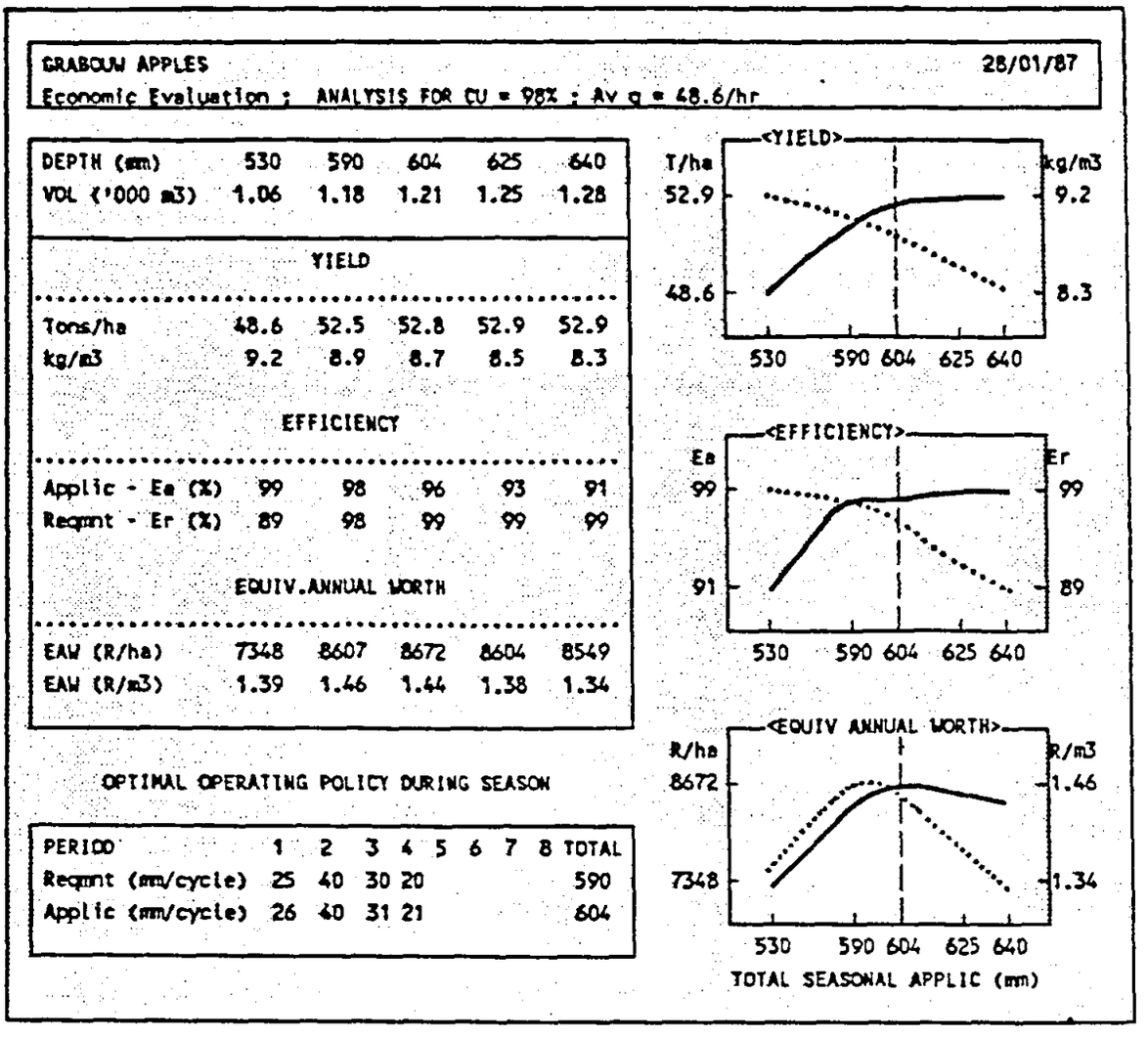


Figure 5.4 : Results from the cost/benefit analysis of the block design evaluation model

2.6 Chapter 6 : Mainline Design

The mainline design problem consists of three distinct elements,
namely :

* The network layout;
* The sequencing (or scheduling) of the valves during operation; and
* Sizing of the pipes and pumps.

These three problems are inter-dependent, so that the solution to any one problem will affect the results of the other two. It is therefore difficult to establish a global optimum solution to the whole design problem. For this reason, the approach adopted has been to develop locally optimized solutions for each module, which can then be modified by a manually directed iterative process, based on the results obtained in each of the other design modules.

2.6.1 Network Layout

The layout problem consists of finding the lowest cost arrangement for connecting the source to each block valve.

In its simplest form, the solution to this problem might be seen to be the layout for which the total length of piping is minimized. However, there are trade-offs in the pipe sizing problem which involve exploiting the prevailing topography to offset pressure losses due to pipe friction. These may mitigate against selecting the shortest path layout. Thus the optimal layout is one for which both the capital costs of the pipes and the energy requirements for operation are minimized.

A practical optimization procedure has proved difficult to establish, since the number of possible layouts for any given situation is theoretically infinite. The proposed procedure entails the designer specifying a layout, which is then subjected to a rapid evaluation by the computer. The result of this evaluation yields a "first shot" estimate (prior to optimization of the pipe sizing problem) of the capital and operating expenses for the proposed layout. The designer may evaluate several different layouts before selecting a final one for further analysis.

2.6.2 Valve Sequencing

The objectives of the valve sequencing problem are twofold :

a) To minimize the pumping energy required at each irrigation shift.
b) To distribute the flow as widely as possible throughout the network in each shift, thereby minimizing the pipe sizes needed in the network.

This is a difficult optimization problem, which is not readily solved by any known techniques. It is further complicated by the fact that often, practical considerations override any sequencing patterns that may have been logical in order to satisfy the abovementioned objectives. For example it may be required to have blocks of the same soil-type grouped together in each schedule. Alternatively the schedule may be dictated by a pesticide spraying pattern which has an associated drying-off requirement.

The solution procedure therefore aims to produce an approximation of the optimum, which is both close to the optimum and efficient in its derivation. The algorithm developed in the research is based on the concept of the *degree of coincidence* of any candidate valve with the valves already allocated to the schedule under consideration. The degree of coincidence is calculated as the product of the length of a section times the flow in that section in excess of the established minimum flow, summed over all sections in the network. The steps of the algorithm are as follows :

1. The valve with the largest discharge requirement is allocated to the first shift.
2. For each remaining valve its *degree of coincidence* with the allocated valve is calculated and these valves are then ranked in order of increasing coincidence.
3. One valve is allocated to each remaining shift, starting from the valve that has the highest coincidence with the allocated valve and working down in decreasing order of coincidence.

An iterative procedure is now followed, starting with the first shift and then working with each shift in turn :

4. The tolerance, δ_j, by which the total discharge in shift j may deviate from the average shift discharge is set to 0.05 (ie. 5%).
5. The degree of coincidence of each of the remaining unallocated valves with the valves already allocated to shift j is calculated and the valves are ranked in order of increasing coincidence.
6. An allocation is attempted on the basis of :

   Working from lowest to highest coincidence;

   Keeping the total shift discharge less than $(1 + \delta_j)$ x the average shift discharge.
7. If no allocation was possible, then the value of δ_j is increased by 0.05, and the process returns to step 5.

   Alternatively if an allocation was made and $j>1$, then a backwards checking function is performed as follows :

   For each valve already allocated to a previously completed shift, the possibility is examined of improving the allocations by swapping with the valve that was allocated to shift j in step 6. A swap is made if :

* the discharges in each shift after the swap remain within the respective allowed tolerances of the average; and
* the combined degrees of coincidence of the swapped valves with the other valves in the respective shifts is less than for the swapped valves in their original shifts.

If a swap is made, the backwards checking function continues through the remaining allocated valves, with the last swapped valve in shift j as the candidate for the next swap.

8. If the discharge in shift j is now greater than $(1 - \delta_j)$ x the average then the shift is fully allocated. The algorithm returns to step 4 and continues for the next shift. If the shift is not yet complete, then the algorithm returns to step 5 and the process is repeated.

The whole process continues until all the valves are allocated.

2.6.3 Pipe and pump sizing

A trade-off exists between the pipe and pump sizes. The higher the pump pressure (higher pumping costs), the greater the amount of pressure that can be lost through friction in the pipes and hence the smaller the diameters (and the cheaper the cost) of the pipes needed in the network. By carrying out a present value analysis on the cost of pumping over the expected life of the system, the energy costs can be expressed in terms of current Rands per meter of pumping head supplied at the source. The cost of the pipes can be expressed in terms of current Rands per meter length of each diameter used in each pipe section. The problem can then be formulated as a *linear programming problem* (LPP), as follows :

* For each section ij of the network, a set of candidate diameters, m, is defined.

* The **decision variables** are then :

  X_{ijm} = the length of each candidate diameter used in each pipe section ij;

  XPM = the maximum pumping head available from the source pump;

  $XP(l)$ = the pumping head provided at each schedule l.

* The associated **costs** for each unit of the decision variables are respectively :

  C_{ijm} = the cost per meter length of pipe of diameter m.

  $K(l)$ = the present value cost per meter pumping head of operating the pump during schedule l

* The **objective function** is given by :

$$\text{Min[K]} = \sum_{ij} \sum_{m} C_{ijm} X_{ijm} + \sum_{l} K(l) XP(l) \qquad (5)$$

Where $\sum_{l}$ = the summation of all schedules l;

$\sum_{m}$ = the summation of all candidate pipe diameters, m, for pipe ij.

$\sum_{ij}$ = the summation of all pipes ij.

K = the total (present value) cost of the system.

* There are four **constraints** as follows :

  Non-negativity, implying that the decision variables must all be non-negative.

  Head loss, implying that for each valve, the combined head loss due to pipe friction and topographic differences, between the source and the valve, must not be greater than the difference between the source pressure and the required pressure at the valve.

  Length constraint, which stipulates that the total length of all the candidate diameters in each section must add up to the length of the section.

  Pumping head, which implies that the operating head in each schedule must not be greater than the maximum capacity of the pump.

Solving this LPP yields the optimum pipe diameter for each section of the network, together with the optimum pumping pressure at the source. If required, the problem formulation can be expanded to incorporate the inclusion of booster pumps. The operating pressure head of the booster pump becomes an additional decision variable in the objective function; and this pressure head is included in the calculations of the head loss constraint for affected valves.

2.6.4 The computer models

A synoptic map of the computer models for mainline design is shown in appendix 1. The programs are menu driven, with data input at each stage being in a tabular, fully editable format rather than on a line by line basis.

Figures 6.1 and 6.2 illustrate the output from the quick layout evaluation process. Figure 6.1 shows the details of each pipe section : connecting points, length, material, expected maximum operating pressure, first shot diameter selection and estimated cost. The selected diameters can be edited by the user and the new costs will be displayed immediately.

PROJ : GO 824 EVALUATION OF LAYOUT 1 : PIPING COSTS

Sect.	From	To	Length (m)	Material	Max Q (m3/hr)	Max H (m)	Class	Diam (mm)	Cost (R)
1	Srce	V 4	10.0	PVC	47	42	6	160	172.60
2	V 4	V 2	50.0	PVC	47	42	6	160	863.00
3	V 2	V 1	82.0	PVC	14	41	6	63	387.04
4	V 2	V 3	72.0	PVC	44	41	6	140	1 110.24
5	V 3	V 5	82.0	PVC	44	39	6	125	1 116.02
6	V 5	V 6	10.0	PVC	44	38	6	140	154.20
7	V 6	V 7	50.0	PVC	33	38	6	125	680.50
8	V 7	V 8	142.0	PVC	33	37	6	110	1 817.60
9	V 8	V9A	142.0	PVC	27	35	6	110	1 817.60
10	V9A	V9B	25.0	PVC	27	33	4	110	230.75
11	V9B	V10	187.0	PVC	18	33	4	90	1 170.62
12	V10	V11	84.0	PVC	18	32	4	90	525.84
13	V11	V12	84.0	PVC	18	32	4	75	440.16
TOTAL			1,020.0						10 486.17

Figure 6.1 : Results of layout evaluation process in mainline design

Figure 6.2 shows the analysis of energy costs for the proposed layout. The main table shows the expected power and energy requirements for the system for each irrigation schedule, together with the associated yearly and present value costs. Under the main table, ten separate parameters which affect the results in the main table are shown. These parameters can be edited by the user and the effects of any changes will be displayed immediately in the main table.

PROJ : GO 824 EVALUATION OF LAYOUT 1 : ENERGY COSTS

Sched.	Load Factor	Effic. (%)	Power (KW)	Energy (KWHrs/Season)	Seasonal Cost (R/Season)	Discounted Cost (R/m)
1	0.50	75	7	4 832	149	152
2	0.50	75	6	4 227	158	163
TOTAL (MAX) :			7	9 059	297	
CAPITAL/PRES. VAL. COST (R)			2 148		10 563	315

Power Capital Cost (R/KW)	300.00	Load Cost (R/KVA/Mnth) :	15.00
Pumping Hrs/Day :	18.	Fixed Costs (R/Mnth) :	0.00
Pumping Days/Cycle :	5.	Analysis Period (Yrs) :	25.
Pumping Cycles/Season :	15.	Interest Rate (%) :	15.0
Energy Cost (c/KWHr) :	8.	Energy Cost Inflation (%) :	18.0

Figure 6.2 : Results of layout evaluation process in mainline design

2.7 Chapter 7 : Applications of the Block Design and Evaluation Models

A typical apple orchard, located in Grabouw, has been used as a **test case for the design and evaluation models.** A first "base case" design has been carried out, and this has then been used for comparison with the results from a number of sensitivity analyses.

2.7.2 The Design Algorithms

Completion of the designs for this test case provided a good opportunity for making adjustments to the design algorithms. In particular, the mainline for the test caser is situated on a slope of 27%, and proved to contain all of the notoriously difficult elements of **steep slope design.**

Notwithstanding these difficulties, the algorithms performed well, and produced very satisfactory results. The mechanisms for introducing a "choking diameter" and for widening the allowable pressure variation envelope, worked appropriately for the steep slope case. Also, the feature of having the design parameters readily available through a "pop-up" window, proved to be most successful.

2.7.3 Sensitivity Analysis

The sensitivity analysis was divided into two categories. The **first** dealt with variations of the design parameters, and the **second** with variations of the input parameters of the economic evaluation model.

In the first set of tests, the most significant results were obtained for a series of variations of the allowable pressure variation, between 10% and 40%. When considering a 15% analysis period, the system capital cost had little influence on the overall profitability of the scheme and an allowable variation of 10% gave the best return on investment. However, if a shorter term analysis period (5 years) was considered, then the traditional 20% variation was shown to be optimal.

2.8 Chapter 8 : Applications of the Mainline Design Model

Four different farm irrigation mainline networks have been analysed, in order to test both the efficiency of the design routines and the range of different types of applications for which the models can be used. The networks tested were as follows :

1. **Ncera - Ciskei Agricultural Corporation;**
2. **Theron-Treurnicht - Eastern Transvaal;**
3. **Bushbuckridge - Eastern Transvaal;**
4. **Beyers Trust - Western Cape.**

2.8.1 Ncera

The **first** network consisted of a highly ramified network with 24 valves, which had already been designed and installed. The results obtained from re-designing using the computerised model were compared with the original design. This case proved to be a good test for the valve sequencing algorithm. The manual design schedules were significantly improved on by the computer selected schedules, and this results in a reduction in both the capital and operating costs of the network.

2.8.2 Theron-Treurnicht

The **second** network was a real design case that was solved using the computer model. A dam is located in the middle of the farm, with lands both above and below it. The question arises of whether to install a single network, with adequate pumping capacity to supply the upper lands, thereby providing excess pressure for the lower lands and enabling small diameters to be used, or alternatively to install two separate networks, thereby reducing the pumping costs for the lower system. The results showed clearly that although the second option was more capitally expensive, the reduced **pumping costs** rendered the overall **total costs** significantly lower than those for the single network case.

2.8.3 Bushbuckridge

This is a large mainline supplying 17 different regions, all operating simultaneously. The computer model was used to investigate the possible benefits of installing booster pumps along the network. A number of economically beneficial positions for booster pumps were identified.

2.8.4 Beyers Trust

This is an existing network which has developed incrementally over a period of several years. The farm lands are situated well below a supply dam and the irrigation system has operated

satisfactorily under gravity since its initial installation. With the increasing use of the mainline network however, the available pressure at the valves has decreased significantly. The question of whether to install a pump into the mainline was investigated using the computer models.

The computer models were run on the existing pipes, to establish an optimal set of operating schedules. These schedules successfully obviated the need to install a pump.

2.8.5 Conclusions

The computer models for mainline design were extremely successful, and they have in fact been incorporated into regular use in the Consultants' offices. An interesting observation that emerged from the results of the test cases was that common design practice tends to underestimate the effects of energy costs, and existing manual designs are therefore generally smaller than would be optimal if a full economic evaluation was made.

3. SUMMARY AND CONCLUSIONS

3.1 Principal Results

The Authors believe that the work on this project, over the past four years, has contributed to the state of the art in a number of specific areas :

3.1.1 Structuring of the design process

The research has resulted in a complete and formal specification of the irrigation systems design process, *viz* :

* Classification of the requirements of the design process into **system and hardware characteristics**, and identification of the individual components within these two groups;
* Formulation of **three main design modules** (preliminary, block and mainline) incorporating all of the required components;
* Identification of the **specific design routines** within each module;
* Specification of the input, output, **design parameters and design objectives** involved in the execution of each routine; and
* Specification of the **links** between various routines.

An overview of this structure is provided in table 2.1 and figures 2.1 and 2.2, together with the synoptic maps in Appendix 1. Documenting this structure constitutes, to the Authors' knowledge, the first such comprehensive specification of the design process. It provides a reference wherein each element of the design process is placed in its full context; as such it formed an essential first step in the development of the complete design model. The Authors feel further that it will prove to be a useful tool for teaching Irrigation Engineering.

3.1.2 Comprehensive evaluation models

Both the mainline design and the block design modules contain comprehensive evaluation processes which enable the designer :

* to assess the extent to which the design satisfies his objectives;
* to generate alternative designs; and then
* to compare these alternative designs.

Appropriate use of these evaluation models will provide the designer with an insight into the performance of the irrigation system that he has not had up till now.

The models are based on a thorough study of the state of the art in measuring irrigation performance, leading to the formulation of a set of performance parameters which have been incorporated into the models. These parameters are discussed in detail in Chapters 3, 5 and 6 of the Technical Report.

The main evaluation model at the end of the block design process provides the designer with information on :

- the **uniformity of distribution** that will result from the designed system;
- the **expected yield** per unit area and per unit of water applied, that will be attained using the system;
- the **requirement and application efficiencies** that will be achieved by the system;
- the estimated **financial return on investment** per unit area and per unit of water applied, that will be achieved; and
- information on the **optimal application depths** during the irrigation season.

It is important to note further that the principle of evaluation has been incorporated into the *whole* design process. Thus, apart from the *main* evaluation model described above, more *general* evaluation is carried out continuously throughout the design process. The models have been structured so that whenever the designer wants to investigate the effects of possible adjustments to the design, he is able to consider these effects in terms of immediately updated evaluation parameters. For example :

* In the **lateral and manifold design routines** of the Block Design module, the designer has the choice of (a) letting the computer carry out the design, either by the "poly plot" routine or by extrapolation of results obtained from previously desgned pipes, or (b) he may specify the design himself, by inputting the required lengths and diameters. Once the design is complete, the table in which the design details are listed (figure 5.2) is updated with statistics on :
  - the cost of the pipe being designed;
  - the total cost of the whole block;
  - the total length of the pipe being designed; and
  - the total lengths, for the whole block, of each diameter of pipe being used.

  If the designer now wishes to change the design, for example by altering the length of one of the pipe sections used for a specific lateral, he will be able to consider the effect of this change on the cost of the lateral and on the overall block costs. Furthermore, having made the change, he can then obtain a graphical plot or a numeric listing of the pressure envelope, and thereby investigate the hydraulic effects of this change.

* In the **valve sequencing routine** of the mainline design module, once again the designer has the choice of either letting the computer determine the schedules or of specifying his own schedules. Once the valves have been fully allocated, the resulting schedules are displayed in a table which also lists a summary of the flow required in each schedule. If the designer decides to alter any of the schedules, the table is updated and the designer is therefore able to monitor the extent to which the flow requirements in each schedule are balanced.

* In the **quick evaluation of layouts** routine of the mainline design module, the results of this evaluation are presented in two tables. The first lists the estimated *capital* costs of the mainline, based on "first shot" pipe diameter selections (figure 6.1). The second lists the estimated *operating* costs, based on prevailing energy cost tarrifs, the expected efficiency of the pumping system and the rates used for the present value analysis (figure 6.2).

  Both of these tables can be edited by the designer and the effects of any changes will be updated immediately. Thus for example, he can investigate the sensitivity of the overall network cost to changes in any of the selected pipe diameters. Alternatively, he can test the sensitivity of the operating costs to changes in the energy tarrifs or interest/inflation rates.

* Similarly, the **linear programming** routine of the mainline module presents the results of the optimization in two tables; one showing the optimum pipe diameters and their associated lengths for each section of the network, and the second showing the resulting pressures at each valve and at the pump.

  The designer may change any of the selected pipe diameters or their lengths, and the effects of such changes will be shown in the cost summaries and in the pressures table.

3.1.3 New design algorithms.

A number of new or modified design algorithms have been developed. These include:

* the valve sequencing algorithm for mainline design;
* the Dynamic Programming optimization of the irrigation operating point, which forms part of the block design evaluation process;
* the Linear Programming optimization of the pipe diameters and pumping points in the mainline design process. Although this procedure is based on well documented algorithms, it has been modified to provide flexibility in the handling of the candidate

diameters constraint and the question of uniform or varied pumping heads in different schedules.

* the lateral and manifold pipe design procedures in the block design. These are also based on well documented algorithms. However, they have been considerably modified in order to make them efficient and stable for common design situations; as well as to incorporate accurate calculation of the pipe and emitter hydraulics.

3.1.4 Rationalization of the design process

Although the design model does not provide a completely rationalized solution to the design problem at this stage (as discussed in Chapter 1), it does enable the designer to carry out a quantitative study of the various trade-offs involved in the design process. For example :

* the suitability of the 20% allowable head loss criterion can be investigated on a case by case basis ;
* the *maximum yield* criterion can be modified to a *maximum profit* criterion, which allows for the possibility of deficit irrigation ; and
* the ratios of cost vs performance, system vs operating costs and block network vs mainline network costs can also be investigated.

3.1.5 Computer aided design (CAD)

The computer programs have been designed to exploit, to the fullest possible extent, the impact of computer aided *design* (as opposed to computer aided *draughting*) on the general Engineering Design process. The Authors believe that they constitute a significant contribution to the state of the art of CAD in the field of Irrigation Engineering.

3.2 Development of the computer programs

The structuring and design of the computer programs played an important part in the successful development of the design models. The programs evolved in three distinct phases, as experience was gained in the use of computer aided design techniques. These phases can be characterized by the nature of the man/machine interface in each case :

3.2.1 Phase 1 : The original PASCAL programs for emitter selection, block and mainline design, written on the Hewlett Packard 9816 computer

These programs employed a *consecutive input* dialogue, followed by a *unidirectional* operating procedure. This meant that the required data was input on a line by line basis, and the designer then sat back while the computer carried out the calculations. Once the design was complete the designer could study the results in order to decide on any changes he might

want to investigate further. These changes would then be incorporated into a new set of input data and the programs would be rerun from the start, using the new data.

The rigidity of this structure precluded the type of continuous evaluation throughout the design process described in section 3.1.2 above.

3.2.2 Phase 2 : The BASIC programs for mainline design, written on the IBM-PC

These programs employ a *tabular input* dialogue and a *multidirectional* operating procedure. This implies that the data are input through fully editable tables. The designer can make any additions or corrections he wants to the tables, before continuing with the various calculation routines. The results of the calculation procedures are also presented in tables on the computer screen, and the designer can once again edit these result tables for use in any on going calculations. Furthermore, the designer does not have to run the program in a fixed order of steps, but can rather move between the various routines at will.

These programs incorporated the continuous evaluation principles discussed above.

3.2.3 Phase 3 : The PASCAL programs for block design, written on the IBM-PC

These programs are operated by similar processes to those of the phase 2 programs. However, they are considerably more flexible in their ability to move between different routines. The prevailing philosophy is one of letting the user determine the path followed through the program, rather than the program directing the user.

3.3 Conclusions

3.3.1 Main conclusions

* The programs work well and provide their users with the hoped for design capabilities. In particular, the design evaluation process has proved to be very successful.

* The phase 1 programs enabled rapid "number crunching", but their structure did not allow for flexible and creative approaches to the design problem.

* The phase 2 and 3 programs are therefore a considerable improvement on the phase 1 programs. Not only do they enable the designer to create any number of design scenarios, but the continuous evaluation facilitates accurate sensitivity analyses.

* Experience during the course of the research has shown that both the on-line availability of the various evaluation facilities, and the user friendly and interactive man/computer dialogue, encourages the designer to undertake a more broadly based and investigative approach to the design problem than was possible in the past.

* The research team was unable to fulfil the project objectives relating to the *application* of the models (see "Attainment of Objectives" below), because the development of the computer programs required considerably more time than was originally anticipated. However, results obtained from some initial applications indicate that the models have good potential capabilties to provide the type of analyses that were hoped for.

3.3.2 Attainment of Objectives

The objectives of the research, are listed in

* Section 1 (page 5) of this report, which highlights the *principal* objectives;
* Appendix 2 (page 52), which provides the *full* list of objectives, goals and expected output from this research, as specified in the original research contract.

In general terms, the *main* objectives relate to the *development* of computer based irrigation design procedures which incorporate full cost/benefit evaluation into the design process (see objectives (b) and (c), goals (a) and (b) and outputs (a) and (b) in Appendix 2).

These objectives have been fully attained through the models discussed in Chapters 4 to 6 of the Technical Report.

In view of the concern about the level at which the models will be applied, expressed by the Evaluation Committee at the outset of the research, it is important to note that the models are used for real *farm level* situations. They are applied in the design office, using a desk-top personal computer with locally developed databases, rather than on any remote main-frame facility with hypothetical data.

A *second* set of objectives (goals (c) to (f) and outputs (c) to (e) in Appendix 2), relate to the *application* of the models on real design cases in order to :

* characterize South African irrigation design practice;
* develop strategies for (a) optimal selection of irrigation method and (b) optimal design under various conditions.

As mentioned above, these objectives have not been fully met, principally because the development of the design models required considerably more time than was originally anticipated. At this stage, only limited application of the design models has been possible.

3.4 The Future

The Authors hope that the impetus generated by the project will continue along two distinct paths, *viz* :

3.4.1 Technology transfer

It is felt that the results of the research can be applied in the following ways :

* The overall design process, as specified by the detailed structure and all the individual routines, should be **incorporated into common practice.** To this end, the design approaches used in the models should be taught to students of Irrigation Engineering; and the possibility of giving seminars on these procedures, to practicing Designers, should be considered. The Technical Report can be used as a complete teaching manual for this purpose.

  The Authors would like to dispel a common misconception that the computer programs can be operated by unskilled personnel to "churn out" irrigation designs. On the contrary, in order to be used successfully they require a good understanding of both the principles of irrigation design and the principles employed in the various design routines.

* Once the results of more applications have been acquired, they can be used to develop a set of design norms that could form the basis of a **code of practice** for the Industry. For example, recommendations could be formulated on the following :
  - The most appropriate overall system *coefficients of uniformity*, under different conditions;
    Expected *application and requirement efficiencies* under different operating conditions.
  - Allowable pressure variation within a system;
  - Appropriate ratios of block versus mainline and hardware versus operating costs;
  - The most economical pipe sizes to be used in mainlines, with due consideration to the cost of energy in the overall cost of the system.
  - One of the most interesting parameters in this category, as far as the Authors are concerned, is the potential for *deficit irrigation* under varying conditions.

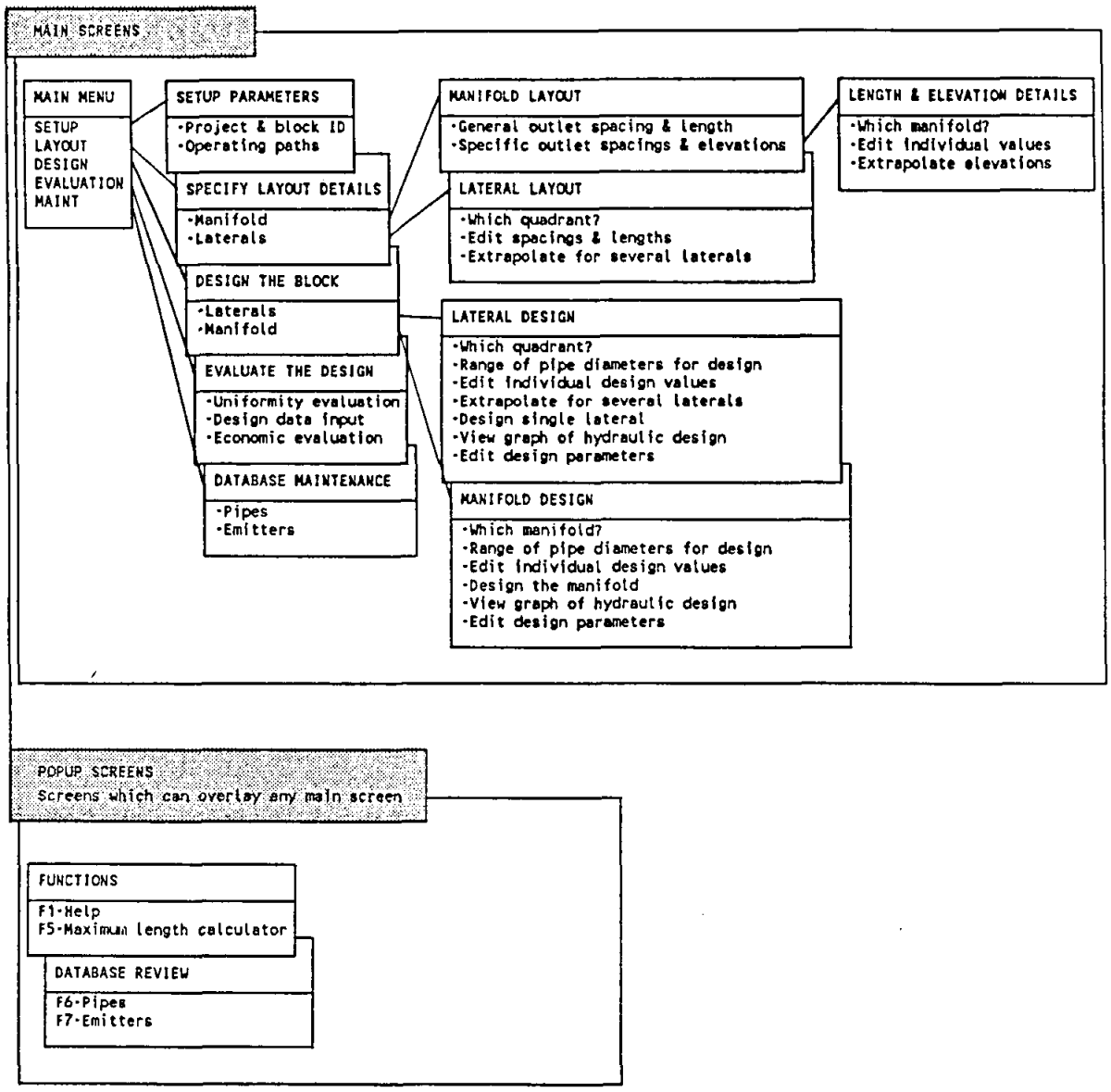
3.4.2 Continued research

The Authors would like to see the research continued in two main areas. The first would involve the application of the models for the development of the design norms discussed above. The second would involve the continued development of the models themselves. This latter aspect of the work would entail :

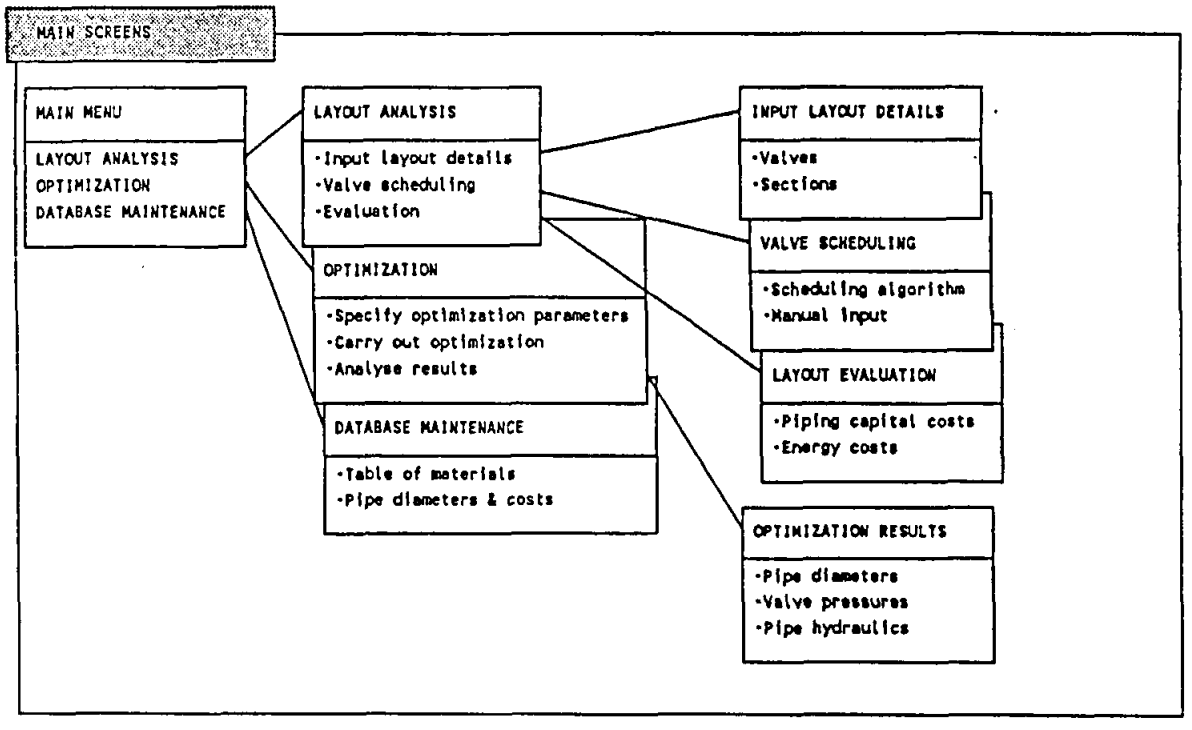
- Integration of all three existing design modules (preliminary, block and mainline) into a single package utilising shared data input and output routines and similar operating procedures.
- Interfacing of the existing *design* package with a computer based *draughting* package, as well as other computer databases; both for the input of data and for the production of final design drawings.
- The development of a complete irrigation equipment database to be used in the design process and also for the drawing up of bills of quantities after completion of a design.

Appendix 1 : Synoptic Maps of the design Models

APPENDIX 1a : Synoptic Map of the Block Design Process



APPENDIX 1b : Synoptic Map of the Mainline Design Process



Appendix 2 : Project Objectives

The Research Contract lists the following objectives, goals and expected outputs from the project :

1. Objectives

The overall objectives of the research will be to develop a comprehensive procedure for the selection of an irrigation method, and for the design of an irrigation system, such that :

a) The selected methodology will be the most appropriate in terms of efficient use of water, energy, labour and other relevant economic factors.

b) The design will consider all system parameters (pump characteristics, local headlosses, flow-pressure relations at each outlet, etc.), and will therefore be accurate.

c) The expected irrigation performance of a given design will be related to the system and its operating conditions, so that the design can be evaluated, in order to enable the selection of optimal systems.

2. Goals

a) To develop a package of computer programs for the design of irrigation systems. These packages will incorporate all aspects of design, including pressure and flow distributions, operating characteristics and costs.

b) To develop a model of the relationship between expected irrigation performance and system characteristics.

c) To characterise existing irrigation practice in several different regions in South Africa, in terms of irrigation performance, cost and utilization of resources.

d) To develop criteria for the optimal allocation of resources for an irrigation system.

e) To develop a model, based on the abovementioned computer package, for the selection from a range of feasible designs of a system which will be optimized in terms of cost and performance.

f) To integrate the results of the abovementioned goals to produce a strategy for the selection of an irrigation method and for the design of an irrigation system, such that the various resources will be optimally allocated and the benefits of the system will be maximal.

3. Outputs of the research

The results of the research will provide the following :

a) A model for rationalized design of irrigation systems.
b) A computerised tool for irrigation system design.
c) A classification of irrigation practice in South Africa, both on a geographical basis and in terms of levels of efficiency of resource utilization.
d) A comparison between different irrigation methodologies in South Africa, in relation to their efficiencies of resource utilization.
e) Strategies for the selection of appropriate irrigation methods and for the optimal design of irrigation systems.