Ion-selective Electrode Determination of Sulphide Produced by Sulphate-reducing Bacteria

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Anaerobic sulphate-reducing bacteria of the *Desulfovibrio* species are widely distributed and cause concern by their corrosion of a wide variety of materials.[1] The bacteria derive their energy from the anaerobic reduction of sulphate (MSO_4) accompanied by simultaneous oxidation of organic substances (C)

$$nC + MSO_4 + H_2O \rightarrow M(Ac)_2 + CO_2 + H_2S \quad .. \quad .. \quad (1)$$

The hydrogen sulphide product provides a means for monitoring the presence and growth of the bacteria and this is the basis of tests recommended by the American Society for Testing and Materials.[2] Here the sulphide ions produced react with an iron(II) salt in the culture to give black iron(II) sulphide. If the precipitate is not visible, the ASTM test uses the referee iodimetric determination of hydrogen sulphide. Sulphate-reducing bacteria are considered to be absent if the concentration of hydrogen sulphide is less than 50 p.p.m.

Hydrogen sulphide levels of 50 p.p.m. (1.5×10^{-3} M) are well within the range of the sulphide ion-selective electrode[3-5] and it has been shown[6] that the electrode gives a quicker indication of the growth of *Desulfuricans* than the ASTM test. This investigation is aimed to provide further information on the scope of the sulphide ion-selective electrode for detecting and monitoring the growth of these microbiological species in various inorganic sulphur sources as growth energy suppliers. The *Desulfovibrio* species studied are *D. vulgaris* (No. NCIB 8457, 1975), *D. desulfuricans* (No. NCIB 8307, 1979) and *D. gigas* (No. NCIB 9332, 1979).

Cultures and Monitoring Assemblies

The supplied batches of *Desulfovibrio* species (obtained from NCIB, Torry Research Station, Aberdeen) were revived in a slightly modified version of Postgate's medium for sulphate reducers as previously described.[6] This (the basal medium) contained 0.25 g of dipotassium hydrogen orthophosphate, 0.50 g of ammonium chloride, 0.50 g of yeast extract, 1.00 g of magnesium sulphate heptahydrate, 0.50 g of sodium sulphate, 0.05 g of calcium chloride dihydrate, 2.5 cm^3 of sodium lactate (70% solution *m/m*) and 500 cm^3 of doubly de-ionised water. The pH was adjusted with sodium hydroxide solution, while 0.50 g of sodium mercaptoacetate and 0.50 g of sodium ascorbate were added for lowering the oxidation - reduction potential (E_h), also as previously described.[6]

Sub-culturing involved adding an aliquot of the starter culture of the revived bacteria aseptically to fresh basal medium of appropriate inorganic sulphate content for the various experiments.

Monitoring of the product sulphide was by an indirect and a direct method.[6] In the indirect method the hydrogen sulphide produced was swept from the culture flask by a stream of white-spot nitrogen into a monitoring flask fitted with a sulphide ion-selective electrode and a double junction reference electrode. The monitoring flask contained sodium hydroxide solution (1 M) and ascorbic acid (2% *m/V*).

For the direct method, the culture flask was fitted with a sulphide ion-selective electrode, a double junction reference electrode and a glass combination pH electrode.

Generally, bacterial growth was followed by monitoring the e.m.f. of the sulphide ion-selective electrode against the double junction reference electrode.

Results and Discussion

Indirect Monitoring

Sulphate in the basal medium

For sub-culture experiments with *D. vulgaris* in basal media containing inorganic sulphate, sharp, increasingly negative e.m.f. changes were recorded in the early stages after inoculation. The e.m.f. then remained steady for a while (shelf region) until there was a further change in the negative direction. Such negative e.m.f. changes, relative to the double junction reference electrode, signify an increase in sulphide concentration. For example, for a medium containing 0.564 g of sodium sulphate as the only source of inorganic sulphate, the early e.m.f. changes (first hour) correspond to an indicated change in the sulphide concentration from less than 10^{-13} M to about 10^{-6}–10^{-5} M (attributable to sulphide brought in by the inoculated starter culture bacteria). The pause (shelf region) period, corresponding to sulphide levels of about 10^{-5} M, last from 1 to 3 d according to the age of the starter culture (older cultures are less virile), after which the sulphide levels quickly increase (within a day or two) to about 10^{-3} M and finally settle down after about 7 d at considerably less than 10^{-3} M as the inorganic sulphur energy source is used up. Electrode readings, confirmed by gravimetric analysis of the sulphide produced (Table I), and negative qualitative tests for sulphate on the exhausted basal medium indicate that *D. vulgaris* bacteria completely consume the available sulphate.

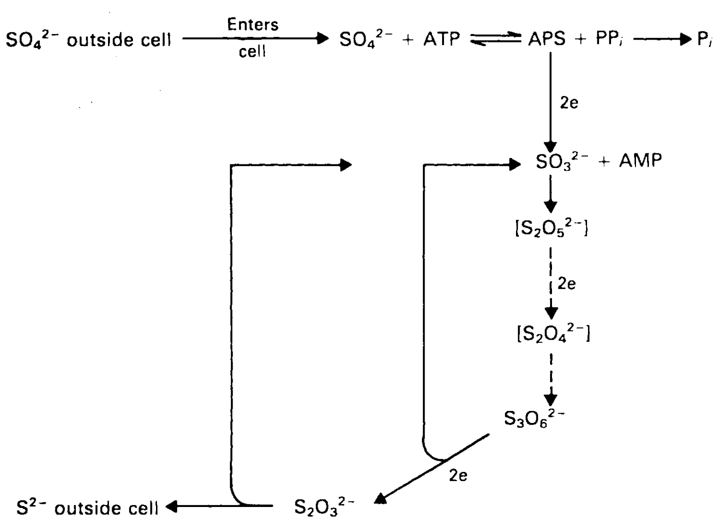
TABLE I

TOTAL SULPHIDE PRODUCTION BY *D. vulgaris* IN MEDIA CONTAINING VARIOUS INORGANIC SULPHUR SOURCES (INDIRECT METHOD)

Sulphur source	Sulphur in medium/g	S^{2-} in monitoring flask/g		Age of inoculum/d	Remarks
		Sulphide electrode	Gravimetric		
0.500 g Na_2SO_4	0.113	0.112	—	10	—
0.100 g $MgSO_4.7H_2O$	0.013	0.012	0.011	42	—
None	—	0.006	None	49	Traces of black ppt. only (from starter culture)
0.564 g Na_2SO_4	0.127	0.128	0.135	73	—
0.500 g Na_2SO_3	0.127	0.124	0.124	201	—
0.500 g $Na_2S_2O_3.5H_2O$	0.129	0.160	0.182	86	—
0.377 g $Na_2S_2O_5$	0.127	0.124	0.137	105	—
0.479 g $Na_2S_2O_6.2H_2O$	0.127	0.0096	None	240	Traces of black ppt. Different ages of starter culture used. No growth
		0.0048		14	
0.564 g Na_2SO_4	0.127	—	0.119	133	Sulphide collected in 2 M NaOH and pptd. as PbS
0.564 g Na_2SO_4	0.127	—	0.115	28	Sulphide collected in $Pb(NO_3)_2$ to ppt. as PbS
0.564 g Na_2SO_4	0.127	0.128	0.118	4	Sodium mercaptoacetate omitted

Inorganic sulphur other than sulphate in the basal medium

The mechanisms of the metabolism of sulphur compounds by sulphate-reducing organisms have been intensively studied. The steps involved in dissimilatory sulphate reduction can be summarised as follows[7]:



In deference to this scheme, studies have been made on sulphite, thiosulphate, metabisulphite and dithionate (not defined in the pathway) as alternative electron acceptor species to sulphate in the basal medium. The masses of inorganic sulphur substrates were so selected that the sulphide collected in the monitoring flask would always be the same, assuming complete consumption. Table I summarises the quantitative sulphide collection data for *D. vulgaris*. It can be seen that sulphite, thiosulphate and metabisulphite are quantitatively consumed.

None of the three *Desulfovibrio* species grew with dithionate in the basal medium. This is not surprising, because the high stability of this species resists the action of most reducing and oxidising agents. Also, the absence of a dithionatase enzyme system may contribute to the metabolic stability of dithionate.

Growth phases for Desulfovibrio types

The pattern of data and conclusions discussed above for *D. vulgaris* also apply to *D. gigas* and *D. desulfuricans* species. In addition, the daily output of sulphide by each of the three species has been monitored by the sulphide ion-selective electrode over periods of 1 month. For these experiments the sodium hydroxide and ascorbic acid components of the monitoring flask were renewed daily. From plots of the daily output of sulphide *versus* time since sub-culture inoculation of the basal medium defined above, it was possible to resolve the various growth - life phases.

The general pattern, apart from a slight initial increase in sulphide at the sub-culturing stage, commenced with a "lag phase," of a few days' duration according to the age of the starter culture. For example, for *D. gigas*, the lag phase was 4 d for 87-d old starter culture, but 8 d for a 153-d old starter culture, while fresher starter cultures gave short lag phases. At the end of the lag phase, the microorganisms multiply with the simultaneous production of large amounts of hydrogen sulphide and are thus in the "logarithmic phase" (for 3 or 4 d), which ends when the culture medium is so altered that it no longer provides conditions for maintaining a uniform rate of growth. At this point the "stationary phase" prevails, when the rate of sulphide production is steady because the organisms cease to multiply. As the sulphate nutrient becomes depleted, the organisms gradually reduce in number and enter the "death phase," until finally the medium becomes sterile. This pattern is consistent with the conclusion of Alico and Liegey,[8] who found that the depletion of sulphate is the major factor contributing to population decline.

Direct Monitoring of Generated Sulphide

The general pattern of growth by this method can be determined from the e.m.f. of the sulphide electrode with respect to the double junction reference electrode. Immediately before inoculating the starter culture into the basal medium containing inorganic sulphate the e.m.f. reading is approximately −300 mV and rapidly alters to approximately −600 mV on introducing the starter culture, before settling down to the "lag phase" value of around −470 mV. In the "growth phase" the e.m.f. gradually changes to values of approximately −600 mV corresponding to the "stationary phase" and the later "death phase."

Quantification of the sulphide in this monitoring method requires appropriate allowances for the hydrolysis equilibria of sulphide to HS^- and H_2S. Such allowances and the response of the sulphide ion-selective electrode activity of sulphide ions, $a_{S^{2-}}$, in the relatively constant ionic strength culture medium, make it possible to calculate the total sulphide species, $[S^{2-}]_T$ from

$$[S^{2-}]_T = f a_{S^{2-}} \qquad (2)$$

where f is a factor for converting sulphide ion activity to total sulphide concentration.

Table II summarises quantitative data obtained by applying equation (2) and confirms the applicability of the direct monitoring method for sulphate as sulphur source. None of the three species was active in the absence of inorganic sulphur, but the thiosulphate was again shown to be acceptable.

It is interesting that organic sulphur, derived here from cystine and cysteine, is acceptable (Table II), the e.m.f. monitoring pattern being as described above. These compounds serve as both the organic nutrient and sulphur source, although the sulphur is already in the −2 oxidation state.

Conclusion

The sulphide ion-selective electrode provides a convenient way of monitoring sulphide produced by sulphate-reducing bacteria, illustrated here by studies on three *Desulfovibrio* species, namely, *D. desulfuricans*, *D. gigas* and *D. vulgaris*. The bacteria also thrive on certain other oxidised inorganic sulphur species that have been shown to be metabolic intermediates, that is, sulphite, thiosulphate and metabisulphite. This wider activity rules out the possible use of the bacteria as practical selective sensors for sulphate.

TABLE II

TOTAL SULPHIDE PRODUCTION BY *Desulfovibrio* SPECIES FROM VARIOUS SULPHUR SOURCES (DIRECT METHOD)

Sulphur source	Sulphur in medium/g	S^{2-} by S^{2-} electrode/g	*Desulfovibrio* species	Age of inoculum/d	Remarks
0.564 g Na_2SO_4	0.127	0.123	*D. vulgaris*	93	—
0.100 g $MgSO_4.7H_2O$	0.013	0.013	*D. vulgaris*	42	—
No inorganic sulphur	—	0.0001	*D. vulgaris*	49	Culture contains 0.50 g sodium mercaptoacetate. No growth
0.564 g Na_2SO_4	0.127	0.134	*D. desulfuricans*	49	—
0.100 g $MgSO_4.7H_2O$	0.013	0.010	*D. desulfuricans*	49	—
No inorganic sulphur	—	0.002	*D. desulfuricans*	32	Culture contains 0.50 g sodium mercaptoacetate. No growth
0.564 g Na_2SO_4	0.127	0.136	*D. gigas*	28	—
0.100 g $MgSO_4.7H_2O$	0.013	0.010	*D. gigas*	152	—
No inorganic sulphur	—	0.002	*D. gigas*	172	Culture contains 0.50 g sodium mercaptoacetate. No growth
0.500 g $Na_2S_2O_3.5H_2O$	0.129	0.122	*D. desulfuricans*	121	—
0.479 g cystine	0.127	0.124	*D. vulgaris*	208	Culture contains no sodium mercaptoacetate and no sodium lactate
0.480 g cysteine	0.127	0.112	*D. vulgaris*	219	Culture contains no sodium mercaptoacetate and no sodium lactate

The various studies show that it is possible directly to monitor the sulphide produced by the bacteria with a sulphide ion-selective electrode. However, in order to distinguish between the "stationary" and "death" phases of the bacterial life span it is necessary to have an indirect method whereby the sulphide-trapping liquid medium in the secondary or monitoring chamber is periodically renewed.

Finally, each of the sulphide ion-selective electrode methods described here is more quantitative than both of the ASTM tests and turbidimetric methods of determining growth of sulphate-reducing bacteria. The turbidimetric method is especially prone to errors because of the clumping of bacterial colonies.

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Interference with Calcium Ion-selective Electrodes by Anionic Surfactants: Studies of Membrane Parameters

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It has been established that the Orion 92–20 liquid membrane calcium ion-selective electrode (ISE) responds, in the absence of calcium ions, to anionic surfactants over limited concentration ranges with an anionic slope.[1,2] Llenado[2] observed that when this electrode was immersed in a solution containing calcium ions and a small aliquot of sulframine (a linear-chain alkylbenzene sulphonate mixture) was added, there was a rapid negative shift in e.m.f. This same rapid, negative e.m.f. shift was also observed for the poly(vinyl chloride) (PVC) matrix membrane calcium ISE,[3] and the present work is concerned with this type of electrode.

The typical response of a PVC matrix membrane calcium ISE based on PVC (0.17 g), dioctylphenyl phosphonate (0.36 g) and calcium bis[di-4(1,1,3,3-tetramethylbutyl)phenyl]-phosphate (0.04 g) to added sodium dodecylsulphate (SDS) is a fall in cell e.m.f. (calcium ISE *versus* saturated calomel reference electrode). This response is linear to log[SDS] up to 4.5×10^{-4} M SDS, after which the e.m.f. response flattens out. Earlier work has shown that the total or partial replacement of the dioctylphenyl phosphonate solvent mediator by decan-1-ol significantly reduces the response of the electrode to anionic surfactants.[3] As this modification can detrimentally affect the selectivity of the electrode to calcium ions, the present study was undertaken to assess the effects of solvent mediators, such as higher alkan-1-ols, tripentyl phosphate and dioctyl phosphite. An alternative approach, based on the total or partial replacement of the PVC matrix with other polymers, has also been briefly studied. The various ISE membrane compositions reflecting alterations in these two parameters are summarised in Table I. These membranes were fabricated and set up into electrodes as previously described.[4]

TABLE I

COMPOSITION OF MASTER MEMBRANES USED FOR PREPARING ELECTRODES

Membrane No.	Composition, including 0.04 g calcium bis[di-4(1,1,3,3-tetramethylbutyl)phenyl]phosphate
I	0.36 g DOPP* + 0.17 g PVC
II	0.36 g Decan-1-ol + 0.17 g PVC
III	0.36 g Dodecan-1-ol + 0.17 g PVC
IV	0.36 g Tetradecan-1-ol + 0.17 g PVC
V	0.36 g Hexadecan-1-ol + 0.17 g PVC
VI	0.36 g Tripentylphosphate + 0.17 g PVC
VII	0.36 g Dioctylphosphite + 0.17 g PVC
VIII	0.18 g Decan-1-ol + 0.18 g DOPP* + 0.17 g PVC
IX	0.18 g Dodecan-1-ol + 0.18 g DOPP + 0.17 g PVC
X	0.18 g Tetradecan-1-ol + 0.18 g DOPP + 0.17 g PVC
XI	0.18 g Hexadecan-1-ol + 0.18 g DOPP + 0.17 g PVC
XII	0.36 g DOPP + 0.085 g poly(vinylidene chloride) + 0.085 g PVC
XIII	0.36 g DOPP + 0.085 g VAGH + 0.085 g PVC
XIV	0.18 g DOPP + 0.18 g decan-1-ol + 0.085 g poly(vinylidene chloride) + 0.085 g PVC
XV	0.18 g DOPP + 0.18 g decan-1-ol + 0.85 g VAGH + 0.085 g PVC

* DOPP = Dioctylphenyl phosphonate.

The data discussed here are based on changes in responses of the various calcium ISEs by bringing various background solutions to 10^{-3} M in sodium dodecylsulphate. For this, the responses of the various calcium ISEs with respect to a saturated calomel reference electrode were assessed in four background solutions, namely 10^{-2} and 10^{-4} M calcium chloride, 10^{-1} M sodium chloride and a buffer solution based on sodium tripolyphosphate formulated to give 1.7×10^{-6} M calcium ions. These background solutions were then spiked with 5×10^{-2} M surfactant solutions until a level of 10^{-3} M in surfactant was reached.

Table II summarises the changes in electrode responses. In general, these show the interference for the 10^{-2} and 10^{-4} M calcium chloride solutions to be approximately the same for each type of membrane (except for added alkylbenzene sulphonate), while the changes in e.m.f. for 10^{-1} M sodium chloride solutions are generally less pronounced and slightly less so again in the sodium tripolyphosphate buffer system.

Solvent Mediator Studies

The replacement of dioctylphenyl phosphonate solvent mediator with decan-1-ol, dodecan-1-ol and tetradecan-1-ol (Table II) significantly reduces dodecylsulphate anionic surfactant interferences with improvement as the alkyl chain is lengthened. The reduced interference, previously noted for decan-1-ol,[3] has hitherto been attributed to the different solubilities of calcium - surfactant complexes in the solvent mediator of the electrode membrane. However, it is also possible that the interference is related to the leaching of solvent mediator from the membrane surface by the surfactant in solution. The supporting evidence for this view is based on the stiffening of samples of membrane I on soaking in SDS solution to indicate the leaching of plasticising dioctylphenyl phosphonate from the membrane. Furthermore, X-ray fluorescence spectroscopy (XRF) studies show a marked reduction in the membrane surface's phosphorus peak following such exposure.

Overall though, the dodecylsulphate anionic surfactant interference is probably due to a combination of various mechanisms, and the increased interference in moving from a C_{14} to a C_{16} chain alcohol in the electrode membrane (Table II) is indicative of this fact.

TABLE II

SURFACTANT INTERFERENCE DATA FOR CELLS WITH CALCIUM ELECTRODES

Membrane No.	E.m.f. changes caused by 10^{-3} M surfactant in solutions/mV			
	10^{-2} M $CaCl_2$	10^{-4} M $CaCl_2$	10^{-1} M NaCl	STP buffer system
SDS surfactant data—				
I	−70 (±3.4)	−68 (±4.1)	−40 (±2.5)	−32 (±6.9)
II	−24 (±2.1)	−25 (±3.0)	−10 (±1.3)	−11 (±2.0)
III	−0.35 (±0.1)	−3.2 (±1.7)	−2.6 (±2.5)	−2.0 (±1.5)
IV	−1.0 (±0.5)	−1.5 (±1.0)	−2.0 (±1.1)	−1.5 (±0.6)
V	−45 (±5.0)	−50 (±3.7)	−32 (±2.1)	−20 (±3.0)
VI	−61 (±3.6)	−65 (±2.9)	−34 (±1.7)	−28 (±4.1)
VII	−75 (±2.9)	−65 (±6.1)	−36 (±3.1)	−44 (±5.1)
VIII	−30 (±1.4)	−40 (±2.1)	−12 (±1.7)	−15 (±2.1)
IX	−24 (±3.6)	−27 (±2.9)	−7.5 (±1.3)	−8.0 (±2.0)
X	−3.0 (±0.3)	−2.1 (±1.2)	−2.4 (±0.4)	−1.3 (±1.0)
XI	−58 (±3.8)	−52 (±2.9)	−35 (±3.7)	−29 (±3.1)
XII	−76 (±4.0)	−79 (±3.6)	−59 (±1.5)	—
XIII	−81 (±3.1)	−95 (±3.9)	−50 (±2.9)	—
XIV	−86 (±6.1)	−82 (±5.2)	−60 (±3.8)	—
XV	−34 (±3.1)	−44 (±2.7)	−38 (±3.1)	—
Tetradecylsulphonate surfactant data—				
I	−65 (±3.0)	−91 (±4.0)	−43 (±2.1)	−23 (±2.1)
III	−1.0 (±1.1)	−72 (±2.1)	−10 (±1.4)	−11 (±2.3)
IX	−21 (±6.1)	−94 (±4.7)	−18 (±3.1)	−13 (±2.9)
X	−2.5 (±0.1)	−124 (±5.1)	−15 (±2.1)	−7.3 (±1.5)
XI	−60 (±2.1)	−99 (±6.1)	−42 (±3.1)	−20 (±2.9)

Polymer Matrix Studies

The data for membranes I and XII–XV (Table II) indicate that the partial replacement of the PVC polymer matrix with either poly(vinylidene chloride) or VAGH (a copolymer of vinyl chloride and vinyl alcohol) does not offer any improvement in electrode behaviour in the presence of dodedylsulphate surfactant.

Effect of Alkylbenzenesulphonate

Changing the anionic surfactant to alkylbenzenesulphonate (ABS) shows an interesting variant of the interference, whereby there is an increased change in the e.m.f. for 10^{-4} M calcium chloride solutions (bottom of Table II). A more detailed study of this surfactant indicates **S**-shaped curves (instead of the normal decrease of SDS) for the change in electrode response with added sulphonate with a point of inflection at 3.5×10^{-4} M sulphonate for membranes I, III, IX, X and XI. The effect regarding 10^{-4} M calcium chloride solutions and the **S**-shaped type of response are both eliminated when the testing is made in sodium tripolyphosphate based calcium ion buffers.

Comparison of the data for dodecylsulphate and tetradecylsulphonate (Table II) shows that the reduction in interference observed for dodecylsulphate in passing to the sodium tripolyphosphate buffer system is not so sustained for tetradecylsulphonate, again indicating that the mechanism of interference may not be simple.

Conclusion

The replacement, total or partial, of dioctylphenyl phosphonate solvent mediator with decan-1-ol, dodecan-1-ol and tetradecan-1-ol offers a basis for improvement in the application of PVC matrix membrane calcium ion-selective electrodes in the presence of surfactants. On the other hand, the use of alternative polymer matrices based on poly(vinylidene chloride) and VAGH copolymer offers no advantage.

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Analytical Aspects of Copper Binding by Humic Substances in Reservoir Sediments

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Humic substances have the ability to form complexes with many metal ions. Of special concern is the formation of water-soluble complexes of the so-called fulvic acids, because they may increase the concentration of metals in natural waters and soils to levels that are in excess of their normal solubilities.

The precise structure of humic acids in unknown, and in any case, varies from source to source, but alcoholic and phenolic hydroxyls, carboxyl and carbonyl groups are known to be present in all types. Undoubtedly, the complexing properties are largely attributable to the phenoxy and carboxyl functional groups.

In this study, humic substances were chemically isolated from organic material collected on the filter beds of certain water treatment plants, operated by the North West Water Authority (Pennine Division). Humic and fulvic acids were separated into several relative molecular mass fractions, in the range $<1 \times 10^4$–7×10^4, by ultrafiltration. These fractions were purified by means of dialysis, re-precipitation[1] and extraction into butan-1-ol.

Interaction of Copper with Humic Substances

Several methods have been used for the study of the binding of metals by humic substances, *e.g.*, ion-exchange equilibrium, electrochemical, flow cell, gel chromatography.

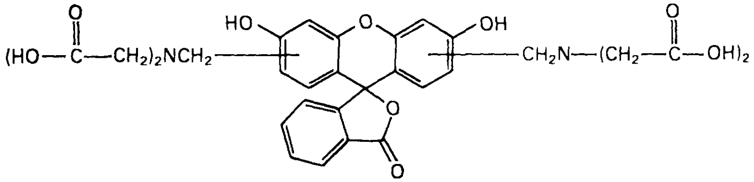
The gel chromatography - complexometry technique is based in the method described by Hümmel and Dreyer[2] and it was first applied to metal - humic substances complexes by Mantoura and Riley.[3] The procedure adopted in the present study is as follows: Sephadex G-15 is equilibrated with a buffer solution containing a known amount of copper. A known amount of humic acid is equilibrated with the same buffer solution and introduced into the column. As the humic acid permeates through the gel, it binds more copper until equilibrium is established. The resultant band of copper deficiency moves more slowly than that of the complex. The concentration of copper in the effluent is then determined and a chromatogram is obtained. An example is shown in Fig. 1. By repeating the experiment with different concentrations of copper, the number of metal binding sites per molecule of humic acid and the stability constant for the complex can be established.

Stability constants in the range 2–4×10^6 have been obtained for copper - fulvic acid complexes which are in agreement with other data obtained for this type of humic substance by workers using different methods.

Lead, cadmium and nickel - fulvic acid stability constants can be determined by using conditions similar to those outlined here.

Determination of Copper by Flow Injection Analysis

The method is based on the quenching of the fluorescence of calcein by copper ions in the pH range 6–9, using an excitation wavelength of 487 nm and an emission wavelength of 510 nm.



Calcein

The commercially available reagent is only of indicator grade and prior purification for its use as a spectrofluorimetric reagent is essential. Re-precipitation and extraction into ethanol are used for this purpose. Excess fluorescein remaining from the synthesis of the reagent seems to be the main impurity; it is not quenchable by most metals and it has a lower solubility in water.

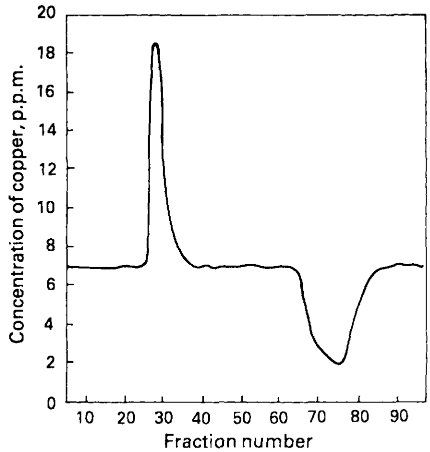


Fig. 1. Gel-permeation chromatogram for the interaction of copper with fulvic acid, $M_r < 10000$.

Bistris {2-[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)propane-1,3-diol} was used for buffering the copper solutions as fractions collected from the GPC column were in that medium. Piperazine-*NN*′-bis-2-ethanesulphonic acid (PIPES) and *N*-2-hydroxyethyl-piperazine-*N*′-2-ethanesulphonic acid (HEPES) were used to buffer the calcein solutions to pH ~6.5 and pH ~7.5, respectively. (The values of their stability constants for the binding of copper are negligible.[3])

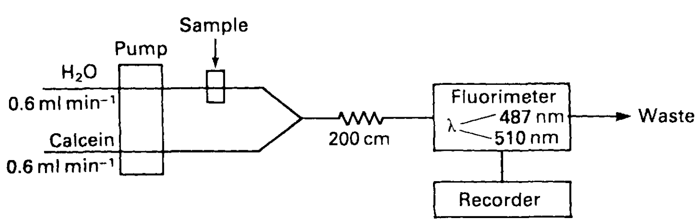


Fig. 2. Manifold for the determination of copper by quenching of calcein.

Fig. 2 shows the manifold that was used. A sampling rate of 30 h^{-1} is possible. The concentration range of copper that can be conveniently determined depends on the concentration of the calcein solution and the medium in which copper solutions are prepared. Copper solutions buffered with PIPES or HEPES produce a similar result to those unbuffered in water. The data are summarised in Table I.

TABLE I

LINEAR RANGE OF COPPER CONCENTRATION DETERMINABLE BY THE QUENCHING OF CALCEIN

Concentration of calcein/M	Concentration of copper $\times$ 10^6/M	
	In water	In Bistris 0.01 M
1×10^{-6}	0.6–4	0.8–5
0.5×10^{-6}	0.1–1	0.2–1

Fig. 3 shows a typical recorder output and the calibration graph for copper solutions in 0.01 M Bistris. The calcein was at a concentration of 1×10^{-6} M in 0.007 M PIPES, pH 6.6. Calcein is not a selective reagent towards copper but for binding studies this is unimportant as the behaviour of only one ionic species at a time is examined. Manganese and lead cause approximately 50% more quenching in an equimolar solution of copper. Iron increases the quenching by only 8%, even at copper to iron molar ratios of up to 1:2.

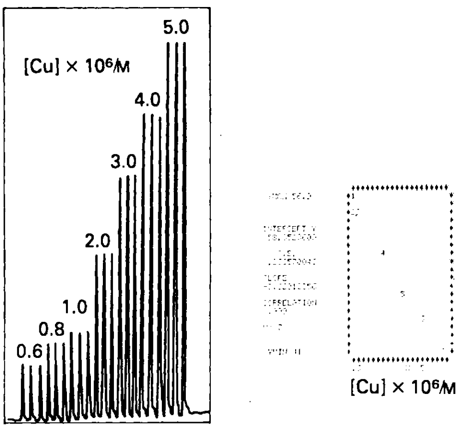


Fig. 3. Recorder output and calibration graph for the copper - calcein determination.

The method could be automated readily due to the simplicity of the manifold used.

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A Versatile Autotitrator using the PET Microcomputer

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Autotitrators[1,2] have been available for many years, but they can be quite expensive, a commercial instrument costing upwards of £5000. The wide availability of microcomputers has made the construction of an autotitrator relatively simple as the complex electronics previously used can be replaced by a computer program. Also, the recent development of cheap, high impedance operational amplifiers and high precision analogue to digital converters (ADCs) has made it simple to input pH measurements directly into a computer.

Apparatus

The main features of the autotitrator system are shown in Fig. 1.

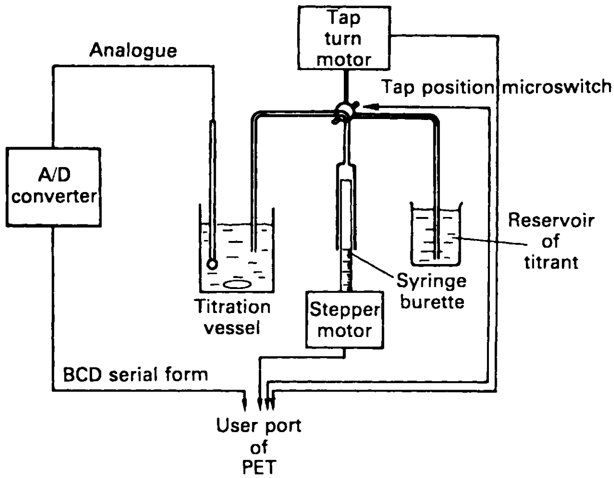

Fig. 1. The Autotitrator system.

The syringe burette. We have used an "Agla" micrometer syringe. It consists of a 0.25 cm^3 precision glass syringe connected to a micrometer screw. For automatic use we drive the micrometer screw with a stepper motor. The smallest micrometer division is 1/50 revolution (0.0002 cm^3), and to turn the micrometer we have used a McLennan ID06 stepper motor with 48 steps per revolution. The circuit for the stepper motor driver is shown in Fig. 2. A series of 5-V logic pulses are applied to point T to turn the stepper motor, and the direction of turn can be altered by setting point R to 0 or 5 V.

A 0.25-cm^3 syringe holds enough for most single titrations, but automatic refilling is advantageous when a number of determinations are being made. The refill mechanism is simply a motor-driven two-way tap.* The tap has a PTFE key fitted with a microswitch, which closes when the bores of the key are in line with the glass ports. One logic pulse sets the motor going. It is turned off again when a 180° turn has been completed. During a titration the

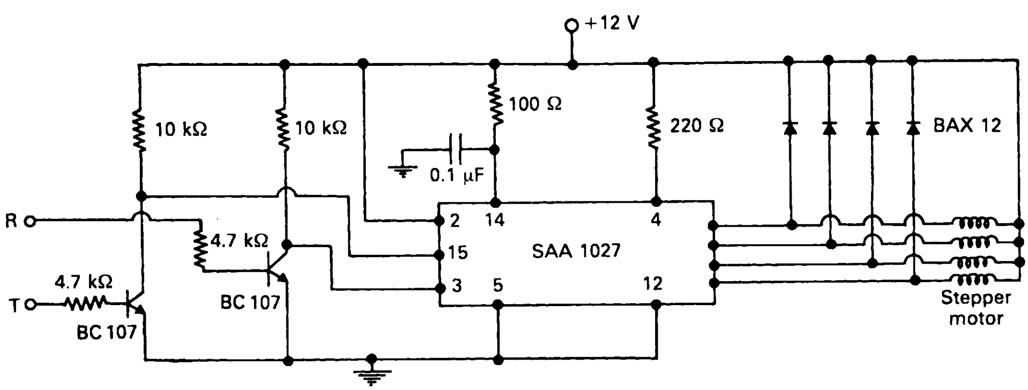

Fig. 2. Stepper motor control circuit.

* A two-way solenoid valve would be equally suitable.

total number of steps turned by the stepper motor is counted, and during the refill cycle the motor is turned the same amount in the reverse direction. This refills the syringe from a reservoir of titrant. The tap then turns through 180° to leave the titrator ready for the next cycle of operations.

Measurement of pH

The glass electrode (or other suitable electrode pair) is connected directly to the input of a **7611** CMOS operational amplifier (Fig. **3**), wired for unity gain ($10^{12}\Omega$ input impedence). The output feeds the ADC. For the satisfactory resolution of pH curves an ADC of 12 bits (giving a resolution of 1 part in 4096) is required. Such ADC devices can be expensive; we have used a very cheap alternative, a **14433** converter, which is designed for use in a digital voltmeter ($10^{9}\Omega$ input impedence). It will carry out a voltage conversion in 0.25 s and gives out digital information as a series of ("$3\frac{1}{2}$") digits coded in binary coded decimal (BCD) to ± 1.999 V.

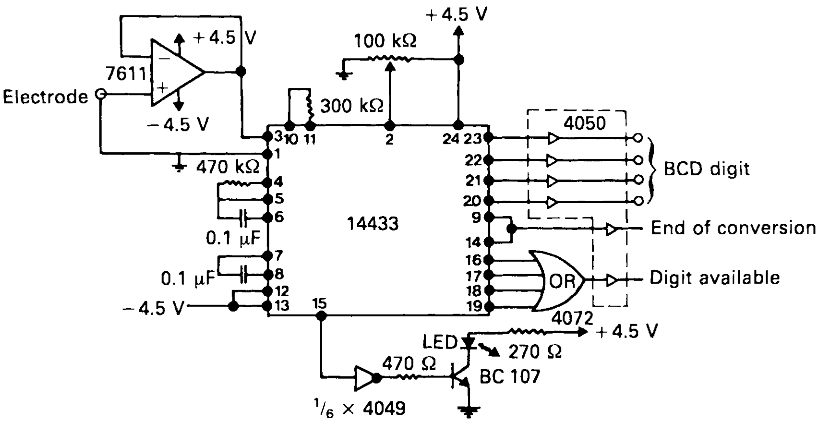

Fig. **3**. Circuit for measuring pH and output of digits to the PET user port.

```
BCD-DRIVER......PAGE 0001

LINE# LOC   CODE        LINE

      0000              ;****************************
      0000              ;*                          *
      0000              ;* BCD CHIP DRIVER ROUTINE  *
      0000              ;*      JRC/DEW  1982       *
      0000              ;*                          *
      0000              ;****************************
      0000              ;
      0000              ; ** NOTE "EOC" BELOW MEANS "END OF CONVERSION"
      0000              ;
      0000              ;
      0000              DDR    = $E843         ;DATA DIRECTION REGISTER OF PET
      0000              PORT   = $E84F         ;USER PORT OF THE PET
      0000              DATA   = $384          ;FOUR LOCATIONS FOR THE RESULTS
      0000              ;
      0000                     *=$388
      0388  78          START  SEI             ;INHIBIT INTERRUPTS
      0389  A9 40              LDA #$40        ;SET ACC = 01000000
      038B  8D 43 E8           STA DDR         ;SET DDR (NOT PA6) TO INPUTS
      038E  AD 4F E8    CYC1   LDA PORT        ;READ USER PORT
      0391  29 10              AND #$10        ;MASK ALL BUT EOC ON PA4
      0393  F0 F9              BEQ CYC1        ;CONTINUE ONLY IF EOC IS HIGH
      0395  AD 4F E8    CYC2   LDA PORT        ;READ USER PORT
      0398  29 10              AND #$10        ;MASK OFF ALL BUT EOC
      039A  D0 F9              BNE CYC2        ;CONTINUE ONLY IF EOC IS LOW
      039C  A0 00              LDY #0          ;SET Y INDEX REGISTER TO ZERO
      039E  20 B2 03           JSR CYC3        ;GO TO READ THOUSANDS DIGIT
      03A1  A0 01              LDY #1          ;SET Y INDEX REGISTER TO ONE
      03A3  20 B2 03           JSR CYC3        ;GO TO READ HUNDREDS DIGIT
      03A6  A0 02              LDY #2          ;SET Y INDEX REGISTER TO TWO
      03A8  20 B2 03           JSR CYC3        ;GO TO READ TENS DIGIT
      03AB  A0 03              LDY #3          ;SET Y INDEX REGISTER TO THREE
      03AD  20 B2 03           JSR CYC3        ;GO TO READ UNITS DIGIT
      03B0  58                 CLI             ;REENABLE INTERRUPTS
      03B1  60                 RTS             ;RETURN TO BASIC
      03B2              ;
      03B2              ;
      03B2              ;***************************
      03B2              ;* READ DIGITS SUBROUTINE *
      03B2              ;***************************
      03B2              ;
      03B2  AD 4F E8    CYC3   LDA PORT        ;READ USER PORT
      03B5  29 20              AND #$20        ;MASK OFF ALL BUT PA5
      03B7  F0 F9              BEQ CYC3        ;CONT IF HIGH : DIGIT PRESENT
      03B9  AD 4F E8           LDA PORT        ;READ USER PORT
      03BC  29 0F              AND #$F         ;MASK ALL BUT PA0-3 :BCD DIGIT
      03BE  99 84 03           STA DATA,Y      ;STORE DIGIT IN $384-7 AS Y
      03C1  AD 4F E8    CYC4   LDA PORT        ;READ USER PORT
      03C4  29 20              AND #$20        ;MASK OFF ALL BUT PA5
      03C6  D0 F9              BNE CYC4        ;CONT WHEN PA5 LOW DIGIT GONE
      03C8  60                 RTS             ;RETURN TO POINT OF CALL
      03C9                     .END

ERRORS = 0000
```

Fig. 4. Machine code routine to read the **14433** analogue to BCD converter chip.

Computation

Reading the pH

The BCD digits produced by the ADC are connected to the microcomputer (a Commodore PET 4032) via the lines PA0–PA3 of the user port. As the BCD digits do not appear on the user port lines for long enough to be read from a BASIC program, a machine-code routine (Fig. 4) is used for this purpose. The routine senses lines PA4 and PA5 to determine when digits are available and the voltage reading is obtained by appropriate addition of the BCD digits. A glass electrode gives a change of about 59 mV per pH unit, and using the equations that describe the relationship between the e.m.f. of a glass - calomel electrode pair and the pH and temperature of the solution in which they are immersed, the e.m.f. reading is converted into a pH value.[3]

The BASIC computer program which controls the autotitrator records the total volume of titrant added and adds increments of a size determined by the rate at which the pH of the solution being titrated is changing. End-points are calculated by looking for the steepest part of the pH - volume-added curve. More sophisticated ways of detecting end-points could easily be included.

The screen of the PET is used, during the titration, to display the volume of titrant added and the pH in the titration vessel. As the pH (or the volume) is in large digits on the screen of the computer it is ideal for demonstrations and other applications where the results are to be viewed from a distance.

The pH electrode and computer, with another simple program, can, of course, be used as a pH meter.

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The Use of Catalytic Thermometric Titrimetry in an Investigation of the Mechanism and Applications of Condensation and Rearrangement Reactions of Mono- and Difunctional Carbonyl Compounds

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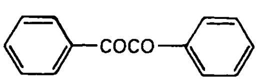
Vaughan and Swithenbank, in 1965,[1] were the first to report on the use of carbonyl compounds as thermometric indicators. They found that when acetone is used as a solvent in the non-aqueous titration of acids a temperature rise occurs at the end-point. In 1974,[2] Greenhow reported on further studies of this phenomenon.

In the present work, mono- and difunctional alicyclic, aryl and alkyl carbonyl compounds and some of their binary mixtures have been evaluated as indicators in the technique based on Vaughan and Swithenbank's original work, and now known as "catalytic thermometric titrimetry."

The relative reactivities of cyclic ketones have been compared by using them as thermometric indicators in the titration of benzoic acid with propanolic potassium hydroxide and noting the sharpness of the end-point inflection and the temperature rise following the end-point (Fig. 1). It was found that the cyclic ketones undergo base-catalysed aldol condensations and the reactivities decrease with increase in the ring size of the ketone.

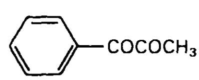
Dicarbonyl compounds evaluated as indicators include benzil (I) and its "homologues,"



(I)

$CH_3COCOCH_3$

(II)



(III)

diacetyl (**II**) and 1-phenylpropane-1,2-dione (**III**). All three undergo an exothermic reaction on titration. The products formed from (**I**) and (**II**) have been identified as benzilic acid, formed by the benzilic acid rearrangement, and a methyl *p*-benzoquinone, formed by an aldol condensation, respectively.

The cyclohexane-1,3- and 1,4-diones, pentane-2,4-dione and hexane-2,5-dione have also been evaluated. Whereas cyclohexane-1,3-dione shows only a gradual temperature rise on addition of the titrant, the -1,4- isomer is much more reactive and a sharp heat rise occurs immediately. While addition of the potassium hydroxide reagent to diacetyl (**II**) produces an immediate temperature rise of about 36 °C, with hexane-2,5-dione the temperature change is about 20 °C and with pentane-2,4-dione, under the same conditions, there is only a gradual rise in temperature. The behaviour of the 1,3-diketones is explained by the resonance stabilisation of the enol form, leading to salt formation with the alkali-metal hydroxides in preference to base-catalysed condensation.

The effect of the nature of the alkali-metal hydroxide catalyst on the rate of these aldol reactions has been investigated using cyclohexanone as the substrate and 0.5-M solutions of sodium, potassium, rubidium and caesium hydroxides in propan-2-ol, and sodium and potassium hydroxides in propan-1-ol, as titrant - catalysts. The thermograms obtained were similar in shape, sharpness of end-point and magnitude of the temperature change. Because, in dilute alcohol solution, the equilibrium

$$OH^- + ROH \rightleftharpoons RO^- + H_2O$$

is displaced to the right,[3] and iso- and n-propoxide ions have similar basic strengths, similar titration graphs would be expected if the metal hydroxides were dissociated to about the same extent in the solvents.

When a mixture of cyclohexanone and n-butyraldehyde is used as the thermometric indicator the thermogram shows two inflections (Fig. 2), and subsequent analysis of the resulting products by GC - MS reveals that the cyclohexanone - n-butyraldehyde cross-aldol condensation and the self-condensation of n-butyraldehyde occur. Formation of the different products was followed by removing samples for analysis during the course of the titration. It was found that the cross condensation reaction to form the mono-substituted cyclohexanone precedes the self-condensation of n-butyraldehyde, which occurs simultaneously with the disubstitution of cyclohexanone. This sequence of reactions supports the "donor - acceptor" theory of aldol condensation.

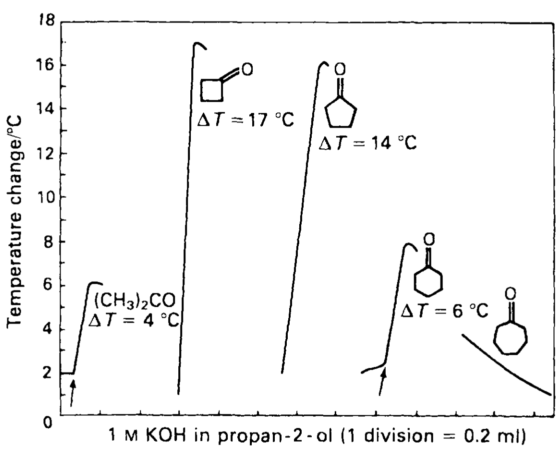


Fig. 1. Titration of acetone and cyclic ketones with 1 M potassium hydroxide in propan-2-ol solution.

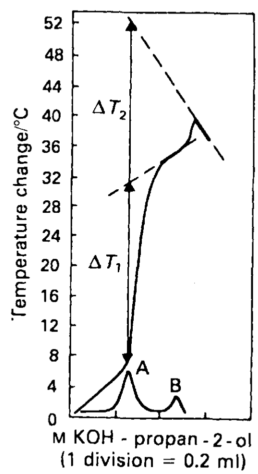


Fig. 2. Thermogram for cyclohexanone - n-butyraldehyde mixture. Peak A, first derivative stage 1; peak B, stage 2.

The heats and rates of reaction of this, and other, mixed systems have been measured conveniently by using the titration curves to provide the data. The heat evolved (Q) was calculated from the relationship

$$Q = \Delta T . c'_p \text{ (joules)}$$

[where c_p' is the total heat capacity of the system and ΔT the temperature change at the end-point (K)]. The heat capacity of the system is obtained by summing the heat capacities of the constituents present at the end-point.

Q can be calculated for the cyclohexanone - n-butyraldehyde reaction (Fig. 2) using ΔT_1 for the first stage and ΔT_2 for the over-all reaction.

The rates of reaction were measured directly by inserting a differentiating device between the bridge circuit output and the chart recorder, in order to record the first derivative of the titration curve (Fig. 2). The rate of reaction (joules s^{-1}) is obtained by multiplying the height of the derivative peak (adjusted to K s^{-1}) by the total heat capacity. For the cyclohexanone - n-butyraldehyde reaction (Fig. 2) there is a derivative peak for each of the two stages. As derivatives cannot be summed, the rate for the over-all reaction cannot be determined directly. Rates were calculated for the separate stages. When the volume of cyclohexanone was kept constant and the volume of aldehyde was varied the rate of the first-stage reaction increased with increase in aldehyde concentration, but the rate for the second stage reached a maximum at a ketone: aldehyde molar ratio of 1:0.87.

The carbonyl compounds were evaluated as thermometric indicators for the non-aqueous titration of some phenols and carboxylic acids. For example, cyclohexanone was used as the indicator - solvent for the titration of dihydric phenols, sterically-hindered phenols and poly-functional benzene carboxylic acids. With it, both acidic functions of 4,4′-dihydroxydiphenyl-methane could be titrated with 1 M potassium hydroxide reagent, but only one of the acidic functions of 2,2′-dihydroxybiphenyl could be determined owing to the strong intramolecular hydrogen bonding between the hydroxy groups. However, the acidic function of the hindered phenol 2,6-di-tert-butyl-4-methylphenol was titrated under the above conditions. The measured reaction stoicheiometry in the titration of polyfunctional benzene carboxylic acids depends on the solubility of the acid salts in the titration media. Thus, benzene hexacarboxy-lic acid in cyclohexanone titrates as a monofunctional acid because the monopotassium salt is insoluble. Addition of certain polar solvents increases the measured reaction stoicheiometry, and with dimethyl sulphoxide as a co-solvent all six carboxylic acid groups can be determined. Hemimellitic acid dihydrate and its salts are sufficiently soluble in cyclohexanone, or rather the mixture of cyclohexanone with the titrant solvent, for all three of the acidic functions to be titrated.

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Mechanism of Metal Sorption from Aqueous Potassium Thiocyanate by Polyether Type Polyurethane Foam

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Bowen[1] first reported the use of polyurethane foams for absorbing various inorganic and organic compounds in 1970. Various reviews have discussed subsequent work concerning their versatility for pre-concentrating and separating a wide range of materials, especially metal ions and organopesticides.[2–5] The studies with metal ions have shown interesting sorptions from potassium thiocyanate solutions[6] matching those by polyether systems.[1,7] Such sorptions (about 1.5 mol kg^{-1}) are frequently considerably greater than can be expected from sorption according to normal surface area considerations (about 3×10^{-4} mol kg^{-1}) of the polyether-type polyurethane foam employed. Therefore, fresh studies have been carried out in order to obtain further evidence of the nature of the mechanism of sorption of metal ions by foam from thiocyanate solutions.

Sorption Mechanisms

A possible mechanism for sorption by polyurethane foam from thiocyanate solution is a simple ether type of solvent extraction, which for cobalt would be

$$2K^+ + Co(NCS)_4^{2-} \rightleftharpoons \{(K^+)_2[Co(NCS)_4^{2-}]\}_{Aq} \rightleftharpoons \{(K^+)_2[Co(NCS)_4^{2-}]\}_{Foam} \quad .. \quad (1)$$

However, sorption by polyurethane foam is much greater (Table I) than by diethyl ether, so that other considerations probably apply.

TABLE I

DISTRIBUTION COEFFICIENTS FOR METAL IONS ON D2 POLYETHER POLYURETHANE FOAM AND FOR DIETHYL ETHER AND BUTYL ACETATE

Initial level of M^{n+} = 0.0025 g in 100 cm³ aqueous 0.6 M KSCN.

	M^{n+}					
System	$CoCl_2$	$FeCl_3$	$Zn(NO_3)_2$	$CdCl_2$	$MnCl_2$	KSCN
D2 foam (0.5 g)	1564	716	∞	309	50	1
Diethyl ether (100 cm³)	0.02	3.9	1.2	0.18	0.04	0.5
Butyl acetate (100 cm³)	0.02	2.3	15.2	0.15	0.04	0.05

Hamon, Khan and Chow[8] considered three alternative mechanisms, namely, ligand addition or exchange, weak and strong base anion-exchange and the cation chelation mechanism (CCM). Ligand addition or exchange is based on nitrogen and oxygen donor atoms of the polyurethane (L:):

$$\text{Ligand addition: } Co(NCS)_4^{2-} + 2L: \rightleftharpoons [Co(NCS)_4:L_2]^{2-} \quad \ldots \quad (2)$$

$$\text{Ligand exchange: } Co(NCS)_4^{2-} + nL: \rightleftharpoons [Co(NCS)_{4-n}:L_n]^{(2-n)-} + nSCN^- \quad \ldots \quad (3)$$

The weak and strong base anion-exchange mechanism depends on the protonation of the nitrogen and oxygen sites of the polyurethane, leaving the anion associated with the foam phase, $\overline{A^-}$, to exchange with anionic metal complex MeX_n^{m-}

$$H^+ + A^- + \overline{\text{site}} \rightleftharpoons \overline{^+H.\,\text{site}} + \overline{A^-} \quad \ldots \quad (4)$$

$$m\overline{A^-} + MeX_n^{m-} \rightleftharpoons mA^- + \overline{Me_n^{m-}} \quad \ldots \quad (5)$$

Alternatively, there could be a binding by metal species (Me) to the $\overline{^+H.\,\text{site}}$ instead of the simple ion exchange of equation (5).

The CCM alternative approach is based on sorption of counter cations in a manner analogous to the uptake of cations (here K^+) by crown and other polyethers. The extraction of complexes (here, say MeX^{m-}) having cations as counter-ions will then be facilitated:

$$K^+ + \overline{\text{site}} \rightleftharpoons \overline{(K.\,\text{site}^+)} \quad \ldots \quad (6)$$

$$\overline{m(K.\,\text{site}^+)} + MeX_n^{m-} \rightleftharpoons \overline{(K.\,\text{site}^+)_m \ldots\ldots MeX_n^{m-}} \quad \ldots \quad (7)$$

Experimental and Discussion

The above have been assessed in an appraisal of the relationships between complex species in solution and species sorbed by polyether-type D2 polyurethane foam (kindly supplied by Dunlop Ltd., Dunlopillo Division, Hirwaun Industrial Estate, Aberdare, Mid-Glamorgan) Experiments were based on equilibrating 100 cm³ of a potassium thiocyanate solution containing 100 p.p.m. of metal ion in various metal salts [$CoCl_2$, $FeCl_3$, $CdCl_2$ and $Zn(NO_3)_2$] with 0.5 g of the foam. Following equilibration, the potassium and thiocyanate contents of the foam were determined and also the metal ion content of the solutions.

The experimental data were used to calculate potassium to metal and metal to thiocyanate ratios associated with the foam phase at equilibrium. These were compared with the predicted stoicheiometries of metal to thiocyanato complexes for various levels of thiocyanate in solution complexes. The predicted stoicheiometries were obtained from the ECCLES computer program,[9] which has been devised for making such evaluations in the light of published[10,11] stability constant data, for the participating complexes.

For the zinc salt at the concentration (100 p.p.m. of zinc) used, the ECCLES program predicts that the principal species present at 0.1 M thiocyanate are $[Zn(SCN)_4]^{2-}$ and possibly $[Zn(SCN)_3]^-$. These are considered to be the most important in the equilibration interaction with polyurethane foam, and the thiocyanate to zinc ratio of 2.6 falls rather below that for the predicted complexes (range 2.3–3.2 in Table II, with 2.6 at the 0.1 M level of thiocyanate in solution). However, potassium to zinc ratio of 1.4 is consistent with expectations from the predicted complexes (range 1.4–2.1 in Table II).

TABLE II

THIOCYANATE - METAL AND POTASSIUM - METAL STOICHEIOMETRIES ON D2 POLYETHER POLYURETHANE FOAM FOR VARIOUS THIOCYANATE LEVELS IN SOLUTION

Taken: 0.5 g of foam + 10 mg M^{n+} per 100 cm^3 of solution. Thiocyanate data based on elemental nitrogen determination (allowance made for foam nitrogen). Potassium data based on potassium determination (allowance made for KSCN sorption on foam).

[KSCN] in solution	$CoCl_2$		$FeCl_3$		$Zn(NO_3)_2$		$CdCl_2$	
	NCS:Co	K:Co	NCS:Fe	K:Fe	NCS:Zn	K:Zn	NCS:Cd	K:Cd
0.1	2.4	1.6	2.2	0.5	2.6	1.4	3.8	0.2
0.4	2.1	1.5	2.5	0.6	2.6	1.1	7.9	3.9
0.6	2.9	1.7	3.6	0.6	2.3	1.3	5.4	3.1
1.0	3.7	1.7	2.4	1.6	3.2	1.8	4.5	3.9
2.0	2.9	2.2	2.9	2.1	3.2	2.1	4.4	3.2

For the cobalt system at the level of 0.1 M of thiocyanate, the ECCLES program predicts $[Co(NCS)_3]^-$, $[Co(OH)_4]^{2-}$ and $Co(NCS)^+$ to be present in equal amounts and accounting for approximately 90% of all species present in solution. Here it is more difficult to draw conclusions from the potassium to cobalt ratios of Table II. Nevertheless, it is also to be noted that for 1.0 M thiocyanate, the ECCLES program predicts $[Co(NCS)_3]^-$ (57%), $[Co(NCS)_4]^{2-}$ (38%) and $[Co(NCS)_2]$ (5%), which make the values of 3.7 for thiocyanate to cobalt and 1.7 for potassium to cobalt (Table II) fairly realistic.

It is not possible to make ECCLES predictions for the iron system because of the lack of stability constant data for many of the species that could be involved. Also, the much lower sorption of cadmium makes the determination of thiocyanate to cadmium stoicheiometries difficult to the extent that the value of 7.9 for thiocyanate to cadmium (Table II) is unrealistically high.

Conclusion

The data discussed above indicate that the sorptions carried out by the polyether type of polyurethane foam of cobalt(II), iron(III), zinc(II) and cadmium(II) from potassium thiocyanate solution seem to be related to their ability to form thiocyanato complexes. Where comparisons can be made, as for cobalt(II) and zinc, the species involved are consistent with predictions based on solution equilibria. The cation chelation mechanism[8] can well be the operative means for the sorptions, and in this respect it is to be noted that infrared studies show the C–O–C band shifted to 1070 cm^{-1} for the polyurethane foam equilibrated with cobalt(II) in 0.6 M potassium thiocyanate solution compared with 1100 cm^{-1} for the position of the band in non-equilibrated foam.[12] A similar shift (to 1085 cm^{-1}) in the C–O–C band has been observed for polyethoxylate (1110 cm^{-1}) when complexed with barium ions.[13]

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Silicon-intensified Target Camera as a Detector for Cool Flame Emission Spectra

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A new type of imaging photodetector, the vidicon tube, was described by Gloersen[1] in 1958 and its potential in analysis outlined by Margoshes[2] in 1970. By the use of this detector, it is possible to combine the advantages of the photographic plate (recording of an entire image and integration during the exposure time) and the photomultiplier tube (high sensitivity and direct conversion of the light signal to an electrical analog) for spectral studies.

Silicon Vidicon

The heart of the entire vidicon is the small chip of silicon that functions as the target of the vidicon detector. It is a single-crystal wafer on which is grown an array of microscopic light-sensitive diodes. The active area of the target measures 12.5 × 10.0 mm and contains many millions of diodes. Initially an electron beam charges the diodes to a uniform voltage and, during the time taken for a complete scan of the target, there is no significant self-discharge. When incident radiation in the ultraviolet to near-infrared range falls on the diodes, they are discharged, and when the beam scans the target again, an electron current flows to re-charge the diodes to the pre-set potential. This current is directly proportional to the radiation intensity incident on the diodes, and is processed by an on-line computer or microcomputer. Thus, if the detector is used to view a spectrum, an instantaneous record of spectral intensity *versus* wavelength is generated in the computer memory, which can be displayed in the visual display unit of the system and photographed or recorded or stored in the system's memories for various arithmetic operations. The vidicon tube is an integrating device and it can acquire a signal in picoseconds to nanoseconds, depending on the intensity. The signal is captured by all channels of the target simultaneously, even though they are read off sequentially or randomly. Most vidicon tubes are limited to 500 channels, which can be scanned in 32 ms.

Silicon-intensified Target Vidicon (SIT)

The SIT vidicon, or silicon-intensified target camera used in the present study, is essentially the same as the silicon vidicon with the addition of an intensifier stage. The intensifier stage has a photocathode, with S–20 characteristics similar to those used in many photomultipliers. As the light sensitive diodes of the target respond not only to photons but also to fast photo-electrons, photons striking the intensifier cathode can cause secondary emission of fast photo-electrons, which can be accelerated and focused on to the target. The resulting minimum detectable signal is about 15 photons or 2 photo-electrons.

MECA Spectrum Analyser

An SIT camera (obtained from EDT Research Ltd.) has been used as a detector for molecular emission cavity analysis (MECA)[3] to study the molecular emissions of seven elements (nitrogen, phosphorus, sulphur, selenium, tellurium, boron and germanium), generated in a cavity placed in a hydrogen-based flame.

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The system used in this study is shown schematically in Fig. 1 and consists of an electronically controlled moveable cavity,[4] which is used to control the precise residence time of the cavity in the flame and the cooling time between successive injections of sample. The emissions generated inside the cavities are focused on the SIT camera via a grating monochromator, which allows a spectral range of 68 nm to be displayed on the visual display unit of the system. The image of the emission spectrum from the vidicon camera is processed electronically by the console. About 150–300 scans are accumulated each time depending on the emission intensity.

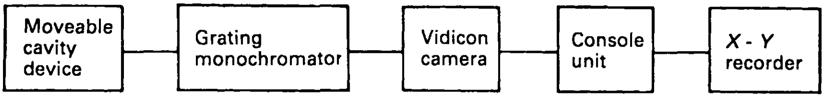

Fig. 1. Schematic diagram of the MECA spectrum analyser.

Fig. 2 shows examples of the spectra detected by the vidicon camera for phosphorus, sulphur, selenium and boron in the visible region of the spectrum.

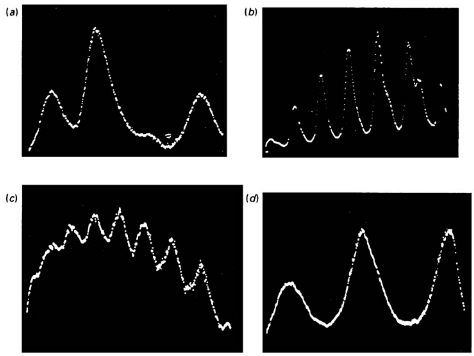

Fig. 2. (*a*) The HPO emission spectrum from phosphoric acid, 502–570 nm; (*b*) the S_2 emission spectrum, 361–429 nm; (*c*) the Se_2 emission spectrum, 446 and 514 nm; and (*d*) the BO_2 emission spectrum from boric acid, 482–550 nm.

The method was found to be fast, easy and more accurate than the previous methods of recording molecular spectra in MECA. The study also showed the potentiality of the vidicon detector in the optimisation of the experimental conditions and its power for the rapid detection of possible spectral interferences.

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