The Analyst

The Analytical Journal
of The Chemical Society

A monthly international publication dealing
with all branches of analytical chemistry

ALAO Volume 100 No. 1188 Pages 145–216 March 1975

THE ANALYST

THE ANALYTICAL JOURNAL OF THE CHEMICAL SOCIETY

Published by The Chemical Society

Editorial: The Director of Publications, The Chemical Society, Burlington House, London, W1V 0BN. Telephone 01-734 9864. Telex No. 268001.

Advertisements: J. Arthur Cook, 9 Lloyd Square, London, WC1X 9BA. Telephone 01-837 6315.

Subscriptions (non-members): The Chemical Society Publications Sales Office, Blackhorse Road, Letchworth, Herts., SG6 1HN.

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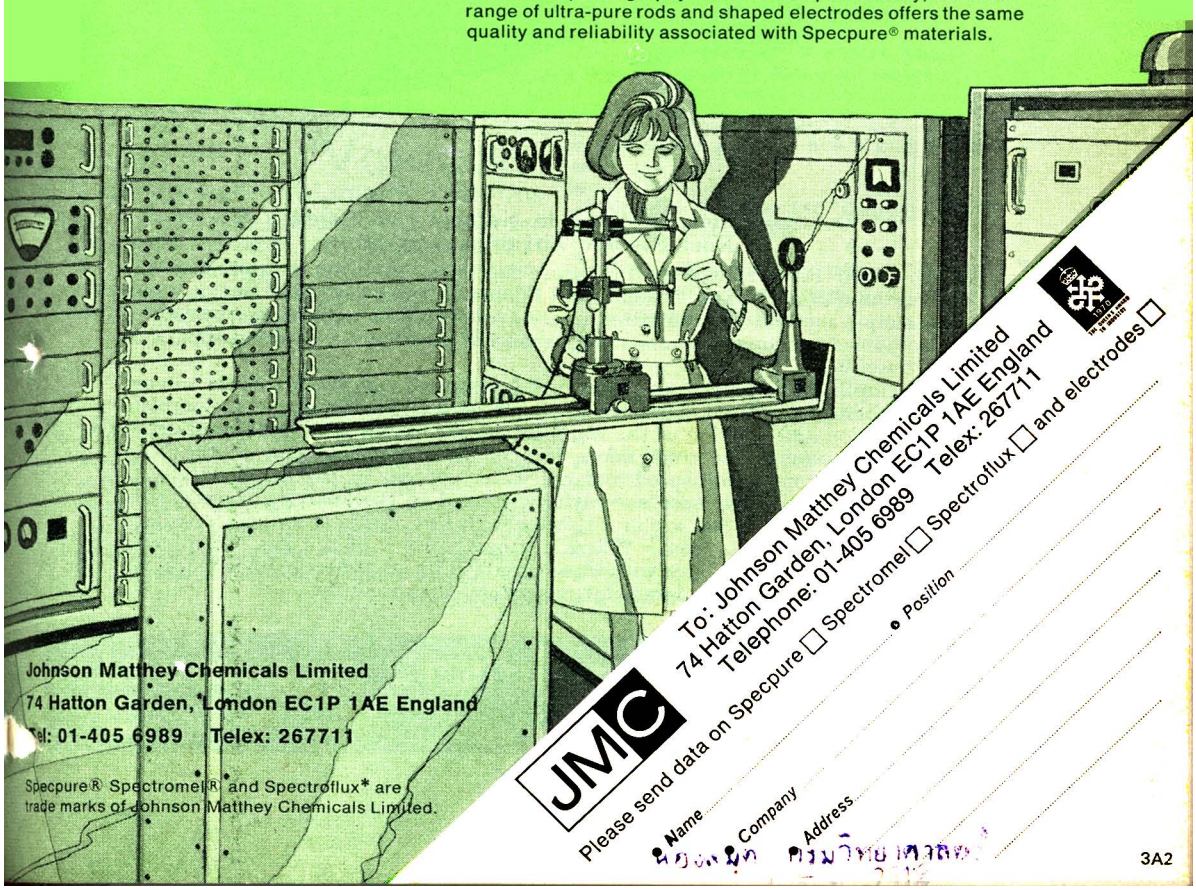

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Summaries of Papers in this Issue

Performance Characteristics of Gas-sensing Membrane Probes

The construction and performance of gas-sensing membrane probes are described and discussed. Experimentally, probes to measure ammonia, sulphur dioxide and nitrogen oxide in aqueous solution have been studied. In particular, the effects of temperature and osmotic pressure were examined, the response speeds of the probes were determined and their use in continuous analysis was investigated. Selectivity is discussed. Consideration is given to the development of new methods of analysis and current applications of the probes are mentioned.

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Electronic Instruments Ltd., Hanworth Lane, Chertsey, Surrey, KT16 9LF.

Analyst, 1975, **100**, 145–156.

A Flow-through Electrode Unit for Measurement of Particulate Atmospheric Nitrate

The design and performance of a flow-through electrode unit for use in the measurement of particulate atmospheric nitrate is described. The unit, housing ion-selective nitrate indicator and fluoride reference electrodes, provides temperature control ($\pm 0{\cdot}5$ °C), a sensitive regulation of solution content ($44 \pm 1{\cdot}5$ ml) and optimum liquid circulation, while minimising liquid volume. Preliminary tests conducted at $38{\cdot}5 \pm 0{\cdot}5$ °C indicate that the unit behaves as an ideal well stirred vessel with a time constant $\tau = V/Q$.

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Analyst, 1975, **100**, 157–162.

The Determination of Water in Natural Gas Using a Modified Karl Fischer Titration Apparatus

The Karl Fischer titration procedure has been extensively applied in the determination of water in solids and liquids, but not in gases. In this paper a simple method for the determination of water in natural gas by use of a modified version of a commercially available Karl Fischer titration apparatus is described.

Sample gas is passed at a known flow-rate through an involatile solvent containing a measured volume of standardised Karl Fischer reagent. Complete absorption and reaction of the water in the gas in and with the Karl Fischer reagent occurs. The time taken for complete neutralisation of the Karl Fischer reagent is measured and the water content of the gas deduced.

The procedure has been successfully applied to the analysis of gases containing from 40 to 200 v.p.m. of water with the results showing a standard deviation of 3–4 per cent. Where the composition of the gas has allowed comparisons, results agree with those obtained by gravimetric, phosphorus(V) oxide cell monitor and dew-point measurement procedures.

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Analyst, 1975, **100**, 163–167.

MARCH, 1975 Vol. 100 No. 1188

The Analyst

Performance Characteristics of Gas-sensing Membrane Probes

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The construction and performance of gas-sensing membrane probes are described and discussed. Experimentally, probes to measure ammonia, sulphur dioxide and nitrogen oxide in aqueous solution have been studied. In particular, the effects of temperature and osmotic pressure were examined, the response speeds of the probes were determined and their use in continuous analysis was investigated. Selectivity is discussed. Consideration is given to the development of new methods of analysis and current applications of the probes are mentioned.

Gas-sensing membrane probes have recently joined ion-selective electrodes in the expanding range of potentiometric sensors for species in aqueous solution, and the probes have been welcomed particularly because of their high selectivity. This paper aims to demonstrate the effect of several parameters on their performance, and to discuss some of the principles upon which they operate. In the light of the performance, consideration is given to the development of analytical procedures using such probes.

Although the first gas-sensing membrane probe was developed for the measurement of carbon dioxide[1,2] in 1957, it was not until more than a decade later that probes to measure ammonia were briefly reported.[3,4] Since then, more development has taken place and the range of dissolved gases for which probes are available has been extended. This range has been discussed by Ross *et al.*,[5] who also proposed a model to explain the effect of some parameters on the performance of the probes.

The probes are a relatively new type of device and hence the problem of nomenclature arises. They sense the partial pressure of gases in solution and thus it is appropriate to describe them as "gas-sensing." As already adumbrated, it is proposed to describe the devices as probes instead of electrodes, as they are electrochemical cells and not simply electrodes in the conventional meaning of the word. Although the term "probe" does not give any information concerning the operation of the devices, it implies a complete system and is brief and not incorrect, as is the word "electrode." It is necessary to add the further word "membrane" to the name in order to differentiate the probes from gas-sensing probes without membranes.[6] Hence the full name that is proposed for the devices is "gas-sensing membrane probes."

A recent paper,[6] in which gas-sensing probes without membranes are described, provokes consideration of the practical advantages conferred by a membrane. The advantages are:

(*a*) The electrolyte layer on the probe tip does not need to be renewed after every measurement in order to maintain accuracy. The membrane serves to retain a bulk of internal electrolyte, which stabilises the composition of the thin film by slow but continuous exchange.

(*b*) As the probe can be immersed directly in the sample, no special equipment is necessary for sample presentation, and the probe can be used in continuous flow analysers.

(*c*) Problems associated with the junction potential at the rim of the electrolyte film will be minimised by the slow but appreciable interchange of electrolyte from the bulk of the filling solution to the thin film.

(*d*) The danger of the probe tip drying out and impairing the performance of the pH-sensitive glass is greatly reduced.

(*e*) The thickness of the electrolyte film can be easily adjusted by alteration of the pressure of the glass electrode on the membrane; this allows simple optimisation of performance of the probe.

(*f*) The membrane protects the internal electrolyte from attack by the air; this is particularly important with the sulphur dioxide probe, in which the thin film of internal electrolyte is susceptible to oxidation. The flow of oxygen into the film is greatly reduced by a membrane.

Gas-sensing membrane probes have found many applications and usually offer a much faster analysis than older methods. With the ammonia probe, satisfactory results have been reported, with respect to precision, accuracy, selectivity and lifetime in the analyses of boiler feed-water,[7–9] fresh waters,[10] blood plasma[11,12] and Kjeldahl digests,[13,14] and also of river water, swimming-pool water, treated and untreated sewage and various trade wastes.[15] In addition to these applications, the ammonia probe is currently used for the analysis of sea water, plating solutions and process liquors in fertiliser manufacture.

The sulphur dioxide probe has many applications in the analysis of food and beverages, boiler water and effluents; in particular, "free" and "total" sulphur dioxide concentrations have been determined in fruit and vegetable products, sausage meat and sucrose and glucose products.

Experimental

Equipment

The gas-sensing membrane probes used were an EIL Model 8002–200 ammonia probe, Model 8010–200 sulphur dioxide probe and a specially developed nitrogen oxide probe. This last probe was constructed from a probe body and glass electrode of the type common to all probes; the reference electrode was a silver wire coated with silver bromide, the internal filling solution was 0·4 M potassium nitrate plus 0·1 M sodium nitrite plus 0·1 M potassium bromide saturated with silver bromide, and the membrane was 0·025 mm thick polypropylene film. The internal filling solution was chosen so as to take account of the potential use of the probe for the determination of nitrates after reduction to nitrite, a process which causes the total concentration of dissolved species in the solutions finally presented to the probe to be relatively high. The reported performance of the nitrogen oxide probe does not necessarily represent the performance of any commercial product.

The probes were used in conjunction with an EIL Model 7050 pIon meter, a Model 8000 automatic monitor and a Model 8981 ion-selective sampling unit. The sampler was a Hook and Tucker Ltd. Model A40 and the four-channel peristaltic pump was a Sage Instruments Inc. Model 371.

Reagents and Standards

All reagents used were of analytical-reagent grade. The water used throughout this work was distilled water, circulated through a mixed-bed de-ioniser.

Ammonia standards were prepared from ammonium chloride, sulphur dioxide standards from potassium metabisulphite and nitrogen oxide standards from sodium nitrite. The buffers added for pH adjustment, in a 1:10 volume ratio unless otherwise stated, were 1 M sodium hydroxide solution, 2 M perchloric acid and 5·4 M sulphuric acid, respectively. The high concentration of sulphuric acid used in this work was unnecessary from the point of view of pH but necessary in order to maintain the correct osmotic pressure; a weaker acid with an inert electrolyte, such as potassium nitrate, added could have been used, *e.g.*, 1 volume of 0·5 M sulphuric acid plus 2·1 M potassium nitrate solution per 5 volumes of sample.

Construction and Operation

The construction, shown in Fig. 1, was identical for the three probes used in this work. The slightly convex tip of the glass electrode is made of pH-sensitive glass. By screwing down the retaining sleeve, the glass electrode can be pressed on to the gas-permeable membrane, and thus a thin film of the internal electrolyte is sandwiched between the glass electrode and the gas-permeable membrane. When the probe is immersed in a sample, gas passes through the membrane until the partial pressures of gas are equal in the thin film and the

sample. The equilibrium concentration of gas in the thin film determines its pH, which is measured by means of the glass electrode and the reference electrode in the bulk of the electrolyte. For ammonia, for example, the pH of the film is proportional to the logarithm of the partial pressure of ammonia in the sample. In the general case, the probe potential is related to the determinand concentration by the equation

$$E = c \pm (2{\cdot}3RT/F) \log_{10} [\mathrm{X}]$$

where X is the determinand, R is the gas constant, T is the temperature, F is the Faraday constant, E is the potential and c is a constant; the sign of the last term is positive for an acidic gas and negative for a basic gas. The derivation of this equation has been published previously.[6,7]

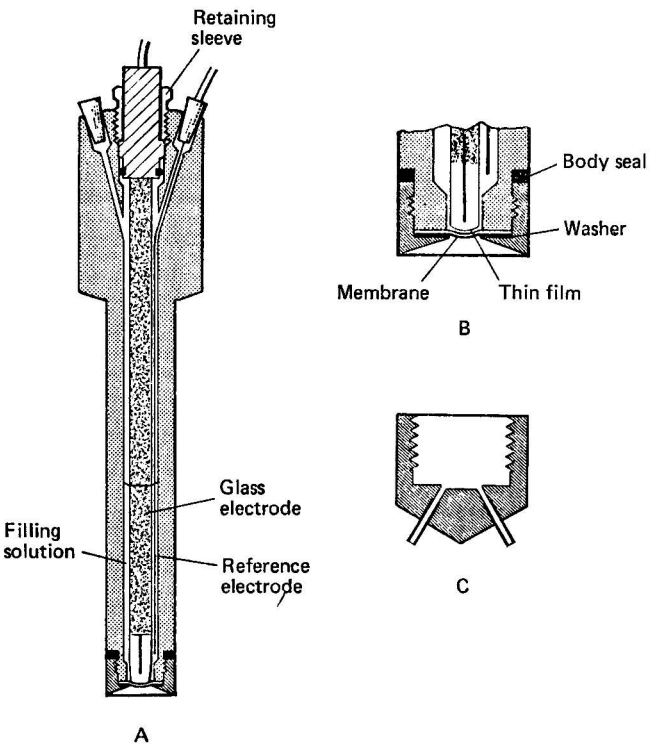

Fig. 1. Construction of probes: A, complete diagram; B, enlarged diagram of end section; and C, flow-through cap.

The fact that only gases in the sample pass through the membrane gives rise to the high selectivity of the devices, but usually also means that sample pre-treatment is required in order to convert the determinand into a form in which it can be measured. Thus, samples containing ammonium ions must be made alkaline and sulphite and nitrite samples acidified before measurement. As the devices sense partial pressure, any parameters that affect the Henry's law constant of the systems will also affect the responses of the probes.

In terms of the equilibria set up in the thin films, the ammonia probe is by far the simplest of the three probes. The nitrogen oxide probe is particularly complicated, with a complex set of equilibria presumably involving at least the five species nitrite ion, nitrate ion, nitrous acid, nitrogen dioxide and nitric oxide; in addition, the various equilibrium constants have different temperature coefficients and some of the species are unstable. Also, in all experiments with the nitrogen oxide probe described in this paper, nitrite ion is considered to be the determinand because it is not known exactly what gaseous species passes from the treated

sample, through the membrane, into the thin film. The imprecise term "nitrogen oxide" in the name of the probe reflects this uncertainty.

Results and Discussion

Calibration and Detection Limit

The varying volatilities and abundances in the environment of the determinands affect the measurement technique, particularly at low concentrations. Thus, when the detection limits and Nernstian response ranges of the probes were measured, particular care had to be taken by use of closed systems. In practice, this situation can be achieved in several ways, some of which are described below. Normally, measurements with the ammonia probe could be made with the samples in open beakers because of the relatively low volatility of ammonia; however, for the calibration runs, a closed flow system (Model 8981 ion-selective sampling unit) was used in order to minimise contamination of the standard solutions with ammonia from the atmosphere. A different closed flow system (as shown in Fig. 4, but without the addition of air) was used with the nitrogen oxide probe. With the sulphur dioxide probe, measurements were made with samples in 100-ml conical flasks; when the probe was immersed in the sample, an O-ring on the probe body sealed the top of the flask. Sulphur dioxide has the highest volatility of the three determinands but the detection limit of the probe is high with respect to the concentration of sulphur dioxide that can normally be absorbed from the atmosphere.

The calibration graphs obtained are shown in Fig. 2. The limit of detection of the ammonia probe has not been determined because the experimental limit is set by the purity of the available water. Similarly, for the nitrogen oxide probe, the limit of detection has not been

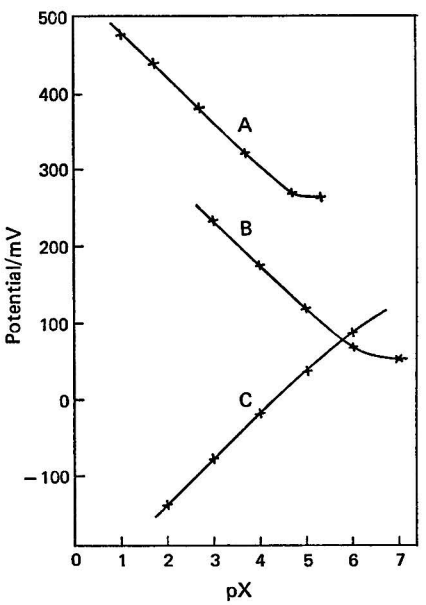

Fig. 2. Calibration graphs: A, sulphur dioxide probe; B, nitrogen oxide probe; C, ammonia probe.

determined because of interference from carbon dioxide (see Selectivity), which it is neither easy nor realistic to exclude. With the sulphur dioxide probe, the detection limit of 5×10^{-6} M (that concentration of sulphur dioxide which produces a shift of 1 mV from the potential of the probe in water) is set by the acidic characteristics of the internal electrolyte.

Response Speed

The response speed of a gas-sensing probe is dependent on several parameters, of which the following are the most important: (*a*) diffusion coefficient of the gas in the membrane; (*b*) partition coefficient of the gas between the membrane and sample; (*c*) membrane thickness; (*d*) geometry of the film of internal electrolyte; (*e*) response time of the glass electrode; (*f*) concentration of determinand; and (*g*) temperature.

A model has been proposed for the effect of parameters (*a*), (*b*), (*c*), (*d*) and (*f*) in the paper by Ross *et al.*[5] Parameters (*a*), (*b*) and (*c*) are controlled experimentally by the choice of membrane, which will be considered further in the section on osmotic effects.

Parameter (*d*) is controlled by the pressure of the glass electrode on the membrane, which can be adjusted by means of the retaining sleeve, and by the shape of the tip of the glass electrode. The model of Ross *et al.* indicates that the thinner the film, the faster the response becomes. A practical limit is reached as a result of the mechanical resistance of the membrane to stretching and increase in the junction potentials round the rim of the glass electrode. The useful limit of membrane tension is reached appreciably before the membrane breaks. In order to produce a film that is very thin across the whole surface of the pH-sensitive glass, it is advantageous to have a slightly convex tip on the glass electrode. This shape has recently been introduced in place of the nominally flat tip used previously and has notably improved response times.

Parameter (*e*) normally does not need consideration as the response speed of the glass electrode is fast with respect to the rate at which equilibrium is reached in the thin film. However, after several months in use, the response of the probe starts to become sluggish because of deterioration in the response of the glass electrode; the continuous use of such electrodes in a poorly buffered medium inevitably leads to a shorter than usual lifetime. The response can be restored by alternate treatment of the glass electrode with sodium hydroxide solution and hydrochloric acid.

The effect of temperature, (*g*), on response speed has not been examined, although it has been shown that the response is faster at higher temperatures; no change in response speed was observed for temperature changes of less than 5 °C.

The response times of the three probes were measured at room temperature (22–25 °C). The definition of response time adopted is the time taken for the probe response to reach a value 1 mV from the equilibrium value after a ten-fold increase or decrease in the concentration of determinand. The solutions, of volume 55 ml, were contained in 100-ml conical flasks and sealed by the probe as described previously. The solutions were stirred at approximately 250 r.p.m. When the probe had reached an equilibrium value in one solution, it was removed from the solution, the flask containing the second solution placed on the stirrer, the end of the probe blotted with tissue-paper and the probe immersed in the second solution. A recording of the probe output was made on a chart recorder, on which the instant the probe was put into the second solution was noted and the final equilibrium value eventually determined. Hence, by chart measurement, the response times were calculated. The time taken to transfer the probe between the two solutions was about 5 s but the probe membrane was exposed to the air for only 1–2 s; the error produced from this source can be estimated, therefore, as a maximum of 2 s, which is negligible in the present context. The results of these response time measurements are presented in Table I.

Using the probes in the flow system shown in Fig. 4, the response times for increases in concentration were similar to those recorded above, but the response times for decreases were substantially greater at low concentrations (less than 10^{-4} M).

In general, the results show that the response is faster at higher concentrations and for concentration increases, as predicted by Ross *et al.*[5] Also, the response times for decreases in concentration are less reproducible than for increases as they partly depend on the time of immersion of the probe in stronger solutions, which affects the uptake of sensed gas into the bulk of the internal electrolyte round the liquid junction.

The response times found for the ammonia probe are shorter than those published previously,[7,10] almost certainly because of the improved shape of the glass electrode mentioned above.

The acceptability of long response times, such as are observed with the sulphur dioxide probe at low concentrations, must be assessed in the light of both the other performance

data and also the time taken for alternative methods of analysis. Even a response time of 5 min in a sulphur dioxide analysis is acceptable if the alternative is a distillation procedure that requires 1 h. The response can be accelerated by changing to a different membrane, but this procedure leads to osmotic problems, which outweigh the advantage.

TABLE I

RESULTS OF DUPLICATE DETERMINATIONS OF PROBE RESPONSE TIMES

	Time/s		
Final concentration/M	Ammonia probe	Sulphur dioxide probe	Nitrogen oxide probe
Decadic concentration increases—			
10^{-5}	105, 110	—	370, 480
10^{-4}	32, 33	425, 335	95, 92
10^{-3}	31, 31	36, 36	34, 38
10^{-2}	31, 30	32, 27	—
Decadic concentration decreases—			
10^{-5}	120, 70	—	460, 410
10^{-4}	66, 34	155, 155	125, 66
10^{-3}	32, 30	68, 42	—

Osmotic Effect

It is inherent in the design of the probes that a semi-permeable membrane separates two solutions, the sample and the internal electrolyte film. If the total concentration of dissolved species differs on the two sides of the membrane, an osmotic pressure difference results and transfer of water vapour across the membrane occurs until the water activity is the same on each side. An osmotic pressure difference also arises when there is a temperature difference between the sample and thin film; as previously pointed out,[5] this difference can lead to very large rates of transfer of water compared with those produced by differences in the total concentrations of dissolved species.

Transfer of water across the membrane will cause dilution or concentration of the electrolyte in the film, which in turn causes the probe potential to drift. Whether or not this drift is observed will depend on whether the change in concentration in the film is fast with respect to renewal of the film by interchange with the bulk of the internal electrolyte. With the ammonia and sulphur probes, drift is not observed if the sample is weaker than the internal electrolyte; for the ammonia probe, if the sample is stronger than the internal electrolyte, then drift does occur. In principle, equilibrium is eventually reached, but in practice this is seldom observed as the system (*e.g.*, the ammonia probe) approaches equilibrium asymptotically over several hours. The magnitude of the drift will depend on both the osmotic pressure gradient across the membrane and also the permeability of the membrane to water.

The nature of the membrane will substantially affect its permeability to water vapour. Two types of membrane, microporous and homogeneous, can be distinguished. In microporous membranes, transfer of gas takes place through the air in the pores of the membrane; the solid material of the membrane is in no sense selective as it merely serves to separate the electrolyte film from the sample. On theoretical grounds, it is not possible to distinguish between the response mechanism of a gas-sensing membrane probe with a microporous membrane and an "air-gap electrode."[6] The ammonia and nitrogen oxide probes contain microporous membranes, the former 0·1 mm thick PTFE and the latter 0·025 mm thick polypropylene. For homogeneous membranes, of which the 0·025 mm thick silicone rubber used in the sulphur dioxide probe is an example, different considerations apply. As suggested by the model of Ross *et al.*,[5] the important parameter is the product (Dk) of the diffusion coefficient of the diffusing species in the membrane (D) and the partition coefficient of the species between the membrane and the aqueous sample (k). The values of Dk quoted by Ross *et al.*[5] show less variation between the different gases in silicone rubber than in air. However, by accepting a slower speed of probe response to the primary gas (sulphur dioxide), the response of the probe to water vapour is made negligible.

In order to determine the magnitude of the osmotic effect with the three probes, the drift rate of each probe was measured in a solution of the determinand in 3 M sodium chloride at a concentration in the middle of the working range of the probe. The values given in Table II are the initial drift rates.

TABLE II

RESULTS OF REPLICATE DETERMINATIONS OF INITIAL DRIFT RATES OF THE PROBES IN SOLUTIONS OF DETERMINAND IN 3 M SODIUM CHLORIDE

Probe	Concentration of determinand/M	Initial drift rate/mV min^{-1}
Ammonia	5×10^{-4}	−12, −19, −14, −22
Sulphur dioxide	1×10^{-3}	0·00, 0·00, 0·01, 0·00
Nitrogen oxide	1×10^{-4}	−2, −2

The drift rate of the ammonia probe decreased steadily over 2 h. If, after returning to samples that did not contain 3 M sodium chloride, the glass electrode was loosened and then re-tightened so as to renew the thin film of internal electrolyte, the probe behaviour reverted to normal immediately.

In the experiments with the sulphur dioxide probe, there was no measurable drift (less than 0·1 mV) over 30 min in three experiments and only 0·2 mV in 20 min in the other experiment; the low drift rate of 0·01 mV min^{-1} is not significant. The probe afterwards responded normally in samples that did not contain 3 M sodium chloride.

The nitrogen oxide probe drifted at the quoted rate for about 5 min; the probe then became very insensitive to changes in the concentration of determinand and the membrane had to be replaced.

There are two alternative means by which osmotic effects due to samples of high dissolved solids content can be eliminated. The first, utilised in the ammonia and nitrogen oxide probes, is to add sufficient inert electrolyte to the internal filling solution to balance the osmotic pressures on the two sides of the membrane. As osmotic pressure is a colligative property, sufficient of the inert electrolyte is added, as a first approximation, to equate the total concentration of dissolved species in the internal filling solution to that in the sample; such a procedure is essential if, for example, an ammonia probe is used to analyse sea water or Kjeldahl digests.[13,14] The second means, utilised in the sulphur dioxide probe, is to select a membrane that is relatively insensitive to osmotic pressure; although this has the disadvantage of reducing the response speed it is, in this instance, the better of the two alternatives because, in practice, the sulphur dioxide probe has many applications in which the osmotic pressure of the sample is not only high but also extremely difficult to assess.

Selectivity

A gas-sensing membrane probe suffers direct interference only from dissolved gaseous species in the treated sample that produce a change of pH in the thin film. That such species are not encountered in most applications is a measure of the high selectivity of the devices.

The ammonia probe has been found to suffer interference only from volatile and filming amines.[7,10]

The sulphur dioxide probe suffers interference from concentrated hydrochloric acid and hydrofluoric acid, but the only analytically important interference is from acetic acid. Interference effects are shown in Fig. 3. This interference prevents the use of the probe for the analysis of low concentrations of sulphur dioxide in pickle products; however, many chutnies and similar products contain sufficient sulphur dioxide to permit dilution of the sample to the level at which interference from acetic acid is negligible. Once severe interference has occurred, the response of the probe becomes sluggish; soaking the probe in water for 15 min and renewal of the thin film are necessary in order to restore performance. Carbon dioxide does not interfere. Oxidising gases, *e.g.*, chlorine, do not normally co-exist in solution with sulphur dioxide. Excess of chlorine in a sample will pass through the probe membrane and destroy the internal electrolyte.

For the nitrogen oxide probe, carbon dioxide is, in practice, the most important interferent and limits the sensitivity of the probe. If the concentration of carbon dioxide in a sample is fixed at 10^{-3} M and the concentration of nitrogen oxide decreased in stages, there is no

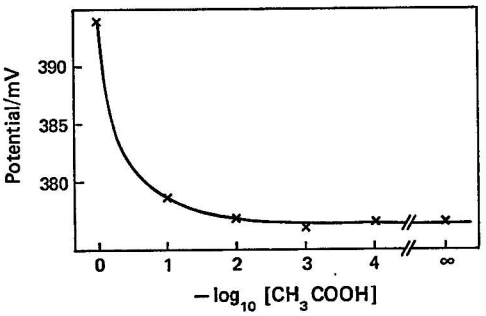

Fig. 3. Interference of acetic acid with the sulphur dioxide probe. [SO_2] = 10^{-3} M.

interference down to 10^{-4} M. However, at 10^{-5} M the probe responds sluggishly and there is a positive potential shift of 8 mV. This result accords with observations, made during the calibration experiments, that the probe drifts to more positive potentials in solutions with nitrogen oxide concentrations less than 10^{-6} M prepared with carbon dioxide free water. Such drift is not observed with similar solutions in equilibrium with the air and, as the equilibrium concentration of carbon dioxide is about 10^{-5} M, this implies a similar selectivity to that indicated above.

Continuous Flow Analysis

The response of the probes is sufficiently rapid for them to be used for the continuous flow analysis of discrete samples. For this purpose, a flow-through cap, shown in Fig. 1 (C), has been designed to fit on to the probe body in place of the standard end-cap. Probes fitted with such flow-through caps were used in experiments with the flow system shown in Fig. 4; samples were separated by appropriate wash solutions in the usual way.

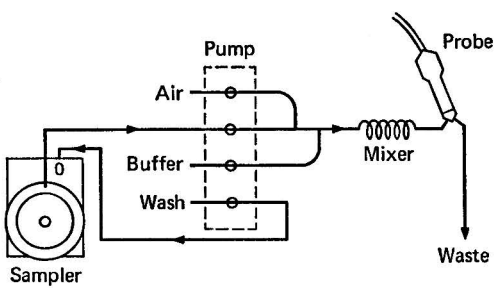

Fig. 4. Diagram of flow system.

Examples of the traces obtained with the different probes are shown in Figs. 5 and 6, ammonia samples being analysed at the rate of 60 per hour and sulphur dioxide samples at 30 per hour. These traces suggest that it is possible to obtain good results at even higher sampling rates, which has been confirmed, *e.g.*, by experiments with the sulphur dioxide probe involving repetition of the sequence of samples shown in Fig. 6 at the rate of 60 per hour.

The ammonia probe has been used in this way in total nitrogen analysis by the Kjeldahl method[14]; after the digestion step, the acidic digest is made alkaline and its ammonia content determined directly with the probe. The sample becomes hot after the addition of alkali and the mixing coil and probe body were therefore immersed in a thermostatically controlled water-bath so as to ensure thermal stability; there is no danger of loss of ammonia because the addition of alkali is made in a closed system.

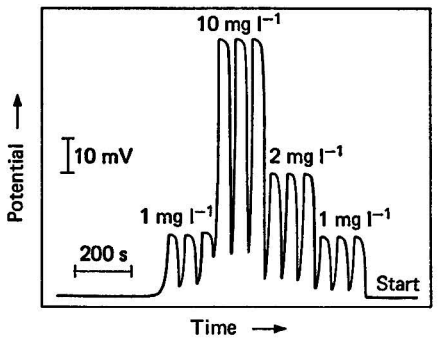

Fig. 5. Response of an ammonia probe in the flow system. Buffer: 0·7 M sodium hydroxide. Wash solution: 0·5 mg l^{-1} NH_4^+. Sampling time: 40 s. Wash time: 20 s. Pumping rates: sample, 4·1 ml min^{-1}; buffer, 0·7 ml min^{-1}; air, 2·0 ml min^{-1}; wash, 4·1 ml min^{-1}.

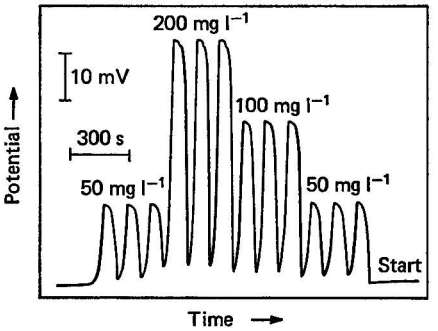

Fig. 6. Response of a sulphur dioxide probe in the flow system. Buffer: 2 M perchloric acid. Wash solution: 25 mg l^{-1} SO_2 (as $K_2S_2O_5$). Sampling time: 70 s. Wash time: 50 s. Pumping rates: sample, 4·1 ml min^{-1}; buffer, 0·6 ml min^{-1}; air, 2·0 ml min^{-1}; wash, 4·1 ml min^{-1}.

Temperature Effects

Because of the complexity of the system, the effect of temperature on the probes is difficult to characterise. The only significant temperature coefficient that can be measured refers to the usually unrealistic state when the probe and sample are both in a thermostatically controlled environment of variable temperature; such coefficients were determined in an EIL Model 8000 automatic analyser. In this analyser, both the buffer and sample are pumped by peristaltic pumps past the probe mounted in a flow cell in a thermostatically controlled cabinet; the temperature in the flow cell is constant to within $\pm 0{\cdot}2$ °C.

The electrochemical cell of which the ammonia probe, for example, consists can be represented by

Ag, AgCl	NH_4Cl (0·1 M) AgCl (s)	NH_4Cl (0·1 M) NH_3 (aq) AgCl (s)	Glass	KH_2PO_4 (0·175 M) Na_2HPO_4 (0·075 M) KCl (0·08 M) AgCl (s) Gelling agent	Ag, AgCl
	Bulk internal electrolyte	Thin film		Glass electrode internal electrolyte	
		Liquid junction			

The different parts of the cell have different temperature coefficients and thermal capacities, and thus the over-all temperature coefficient will apparently vary with time until thermal equilibrium is achieved. The output of the ammonia probe takes much longer than the other probes to reach equilibrium, presumably because an increase in the temperature of the sample induces osmosis, that is, transfer of water vapour into the thin film. As the temperature of the thin film slowly approaches the temperature of the sample, the transfer of water vapour decreases and then reverses in direction until the original electrolyte concentration in the thin film is restored. The second osmotic step is slow and is responsible for the long equilibration time of the ammonia probe. A further problem with the ammonia system is that the equilibrium constant, K, has a high temperature coefficient (about $-0{\cdot}28$ l mol^{-1} $°C^{-1}$) and thus the probe has a high temperature coefficient. If the internal electrolyte of the glass electrode is changed to an ammonia - ammonium chloride buffer, the temperature coefficient is halved, but the drift caused by osmosis remains the predominant temperature effect.

The temperature coefficients for the probes in a Model 8000 automatic analyser are listed in Table III.

TABLE III

RESULTS OF REPLICATE DETERMINATIONS OF THE PROBE TEMPERATURE COEFFICIENTS

Probe	Concentration of determinand/M	Temperature coefficient/mV °C^{-1}	Temperature range/°C
Ammonia	6×10^{-4}	1·5, 1·0	28–35
Sulphur dioxide	1×10^{-3}	0·5, 0·6, 0·5, 0·5	26–43
Nitrogen oxide	1×10^{-4}	0·2	25–31
		0·0, 0·0, 0·0, 0·1, 0·0	31–45

The curves obtained in experiments with the ammonia and sulphur dioxide probes are shown in Fig. 7. The shape of the curve for the ammonia probe was different from the shapes of those for the sulphur dioxide and nitrogen oxide probes, which were similar. The trough in the curve for the ammonia probe can be attributed to osmosis occurring before the probe has reached thermal equilibrium, as discussed above. This result again highlights the advantage of using a membrane that is less permeable to water vapour on the sulphur dioxide and nitrogen oxide probes.

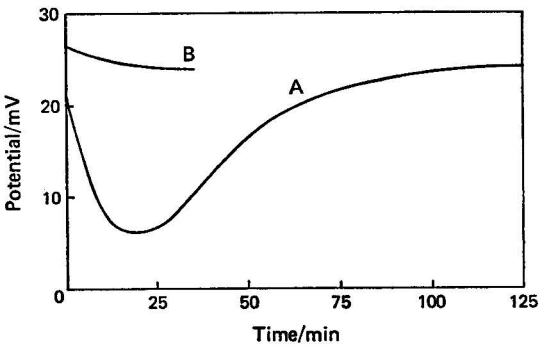

Fig. 7. Curves of potential variation with time obtained after a temperature change for the ammonia and sulphur dioxide probes. A, Ammonia probe: $[NH_3] = 6 \times 10^{-4}$ M; 31·3–34·6 °C. B, Sulphur dioxide probe: $[SO_2] = 10^{-3}$ M; 31·0–36·7 °C.

If a probe is used under laboratory conditions, with the bulk of the probe at room temperature and the samples at varying temperatures, a different behaviour is observed. The apparent temperature coefficient of the ammonia probe increases to about 2 mV °C^{-1} and the sulphur dioxide probe becomes virtually insensitive to temperature. Thus, in the use of an ammonia probe, care must be taken to ensure that standards and samples are kept at the same temperature and that the probe is not subjected to rapid temperature fluctuations, for example by exposure to direct sunlight.

Development of Method

In the development of an analytical procedure involving the use of a gas-sensing membrane probe, there are a number of factors that require consideration; many of these problems have been discussed in previous sections but, for convenience, all of the important factors can be listed as follows: (*a*) sample pH; (*b*) sample temperature; (*c*) sample osmotic pressure; (*d*) state of determinand; (*e*) potential interferents; (*f*) volatility of determinand; (*g*) stirring of sample; and (*h*) standardisation.

(*a*) The pH of samples must be adjusted, if necessary, in order to convert virtually all of the determinand into the state of dissolved gas. For the determination of ammonia, the sample, when presented to the probe, should have a pH above 12. In sulphur dioxide determinations, the pH should be below 0·7; the buffering is achieved by the addition of a non-volatile acid such as sulphuric or perchloric acid. Buffering at a higher pH, at which only a fixed proportion of the sulphur dioxide is present as the dissolved gas, reduces the sensitivity of the procedure and requires precise pH adjustment if accuracy is to be maintained. The same argument applies to the ammonia probe. For the determination of nitrogen oxide, the sample must also be acidified.

(*b*) The temperatures of samples and standards should be as closely similar as possible, ideally within 0·5 °C, so that the Henry's law coefficient is constant throughout the experiment, and so that the probe remains at constant temperature.

(*c*) The osmotic pressure of the sample as presented to the probe is an important consideration in the use of the ammonia and nitrogen oxide probes. In the application of the ammonia probe, the osmotic pressure of the internal electrolyte must be adjusted by addition of inert electrolyte (*e.g.*, potassium sulphate or sodium chloride) if the total concentration of dissolved species in the sample exceeds 0·3 M. As a first approximation, sufficient electrolyte should be added to increase the total concentration of dissolved species from 0·2 M to that of the sample. Often, such adjustment can be avoided by dilution of the sample if the concentration of the determinand permits. Dilution of the sample is advantageous even if it is not possible to make the osmotic effect negligible, as the lower the osmotic pressure the less precisely does the adjustment have to be made. With the nitrogen oxide probe, all samples must be adjusted so as to have a total concentration of dissolved species of $1{\cdot}20 \pm 0{\cdot}06$ M by the addition of an appropriate buffer, as in the experiments described in this paper.

(*d*) In many ammonia samples, a significant proportion of the ammonia is complexed with metals such as copper and zinc. If it is required to measure this complexed ammonia also, EDTA must be added to the buffer; a buffer containing 50 g l^{-1} of sodium hydroxide and 15 g l^{-1} of EDTA added in the ratio of one volume to ten volumes of sample may be used. The use of such a buffer also has the advantage of preventing precipitation of many metal hydroxides that could absorb ammonia and block flow systems.

Sulphur dioxide in many foods and beverages is partly present bound in aldehyde - hydrogen sulphite addition compounds, which are not decomposed by simple acidification. Hence "free" sulphur dioxide can be measured by acidification. "Total" sulphur dioxide can be measured after a preliminary treatment with alkali in order to decompose the addition compounds; decomposition is very rapid at pH values above 12·5. The sample is then acidified, as before, to a pH below 0·7 and the reading of "total" sulphur dioxide made. Recombination of the sulphur dioxide with the aldehydes is very slow compared with the response speed of the probe.

(*e*) The possibility of chemical interference with the probe response must be considered. If possible, interferents should be eliminated.

(*f*) Measurements with the sulphur dioxide and nitrogen oxide probes should, as far as possible, be taken in closed systems. The conical flask arrangement described previously has been found to be satisfactory; alternatively, the use of a closed flow system eliminates any problem due to the volatility of the determinand.

(*g*) All samples and standards must be stirred. In a few instances, such as in the analysis of sausage-meat slurries with the sulphur dioxide probe, vigorous stirring is recommended so as to prevent particles of the sample from adhering to the probe.

(*h*) The accuracy of measurements with a probe is limited by the accuracy of the standards. This is a particularly important consideration with the sulphur dioxide probe, as solutions of potassium metabisulphite or sodium sulphite deteriorate rapidly; hence, for the most accurate measurements, the stock solution should be standardised by an iodine - thiosulphate titration.

The treatment of samples and standards should be identical. It is particularly important to keep the total dilution of samples and standards by buffers the same. If a preliminary treatment is necessary, as in the decomposition of aldehyde - hydrogen sulphite addition compounds in foods, allowance must be made for the increased dilution of the sample.

Although all of these points must be considered in the development of a new method, the resultant procedure will usually be straightforward and accomplished in a much shorter time than by conventional methods.

The authors thank Electronic Instruments Ltd. for permission to publish this paper and gratefully acknowledge the assistance of their colleague Mr. C. L. Jamson.

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Received *August* 1*st*, 1974
Accepted *November* 11*th*, 1974

Analyst, March, 1975, Vol. 100, pp. 157–162

A Flow-through Electrode Unit for Measurement of Particulate Atmospheric Nitrate

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The design and performance of a flow-through electrode unit for use in the measurement of particulate atmospheric nitrate is described. The unit, housing ion-selective nitrate indicator and fluoride reference electrodes, provides temperature control (±0·5 °C), a sensitive regulation of solution content (44 ± 1·5 ml) and optimum liquid circulation, while minimising liquid volume. Preliminary tests conducted at 38·5 ± 0·5 °C indicate that the unit behaves as an ideal well stirred vessel with a time constant $\tau = V/Q$.

The nitrate-selective electrode has been used successfully to measure nitrate levels in soils,[1,2] plants,[3] water[4] and microbiological media,[5] and to determine the concentration of nitrogen oxides in flows of combustion effluents.[6,7] More recently, the nitrate electrode has been introduced into a continuous flow system designed to monitor the atmospheric particulate nitrate as described by Driscoll and Forney.[8]

In this application, a fixed volume of de-ionised water is recirculated through an aerosol impaction device (ERC LEAP sampler, Model 3440) in which nitrate particulate is collected and dissolved. If ideal aerosol collection is assumed, the nitrate concentration, C, within the monitor recirculation volume is given by

$$C \text{ (mol l}^{-1}) = 1{\cdot}61 \times 10^{-5} \frac{\overline{C}Qt}{V_T} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where $\overline{C}$ μg m^{-3} is a time-average atmospheric nitrate concentration, Q l min^{-1} is the air sampling rate, t min is the sampling time and V_T ml is the recirculation volume.

As the nitrate liquid ion exchange is only partially selective for nitrate ions and responds to a number of other dissolved species, as indicated in Table I, it was necessary to determine which of the species were potential interferents in atmospheric particulate. As described

TABLE I

POTENTIAL INTERFERENCES IN THE NITRATE ELECTRODE METHOD OF ANALYSIS[8]

$K_x = 1{\cdot}0$ for NO_3^-.

Species	Selectivity constant[8] (K_x)	Present in atmospheric particulate
ClO_4^-	10^3	No
I^-	20	Yes
ClO_3^-	2	No
Br^-	0·13	Yes
HS^-	0·04	Yes
NO_2^-	0·04	Yes
CN^-	0·01	No
HCO_3^-	9×10^{-3}	Yes
Cl^-	4×10^{-3}	Yes
CH_3COO^-	4×10^{-4}	No
CO_3^{2-}	2×10^{-4}	Yes

by Driscoll and Forney,[8] two of the most serious interferents, perchlorate and chlorate, are not present in atmospheric particulate while anticipated levels of bromide, iodide and sulphide were eliminated by using a 10^{-2} M silver fluoride collection solution. Thus the silver ion eliminated the potential halide and sulphide interferences while a source of fluoride was provided for a fluoride reference electrode (see Fig. 1). Preliminary atmospheric tests using the monitor indicated that the device yields nitrate levels comparable with those from standard sampling techniques (*e.g.*, high volume sampling with wet-chemical filter analysis[8]) with substantial savings in time.

This application of the nitrate electrode necessitated the design and evaluation of a continuous flow-through electrode unit that provides several simultaneous functions. Briefly, these functions are reproducible stirring of the test solution, a constant temperature, a steady liquid level or recirculation volume, a minimal solution volume, provision for solution inflow and outflow and housing for the necessary instrumentation. After a critical review of existing flow-through units, in particular those described by Růžička and Tjell[9] and Milham,[10] it was found that none adequately provided all of the necessary functions. It is the purpose of this paper to describe in detail the design and evaluation of the flow-through electrode unit.

Instrument Design

A schematic diagram of the nitrate monitor as discussed in detail in a Walden Research Division Report,[11] including the flow-through unit, is shown in Fig. 1. The electrodes used were the Orion Model 92–07 nitrate electrode, used as indicator, and Model 94–09 fluoride electrode, used as reference, with the voltage difference indicated by an Orion 701 digital pH/mV meter.

Housing

The housing of the flow-through unit was machined from a solid cylindrical block of lucite. This arrangement provided a sturdy, transparent dielectric cell that was easy to adapt to the dimensions of the probe.

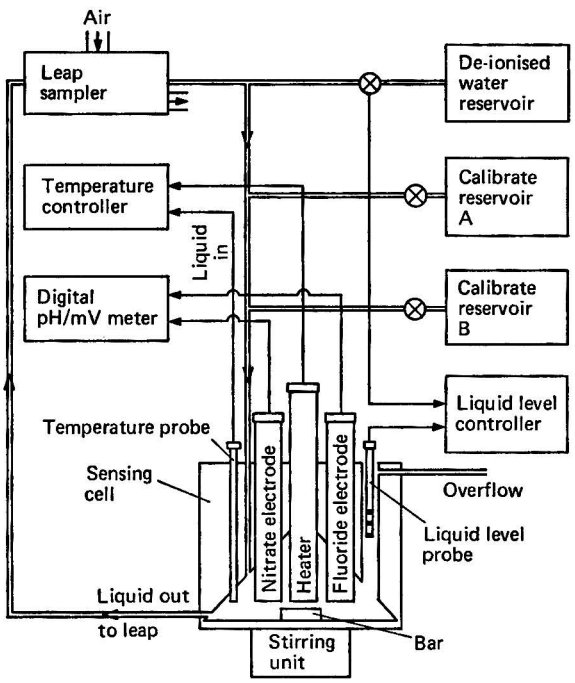

Fig. 1. Schematic diagram of flow-through electrode unit and associated nitrate monitor instrumentation.

As seen in equation (1), the response time of the monitor is inversely proportional to the recirculation volume. As a large fraction of the fluid resides within the flow-through electrode unit, a small solution volume was sought, which, at the same time, would provide adequate circulation. An optimum design, indicated in Fig. 1, was found to be a solution cavity in the shape of an inverted cone. This design provided both solution depth and sensitivity to small changes in liquid level, while allowing for free circulation at the base

of the cavity. The solution volume was determined to be $V \approx 44$ ml with probes, electrodes and stirring bar inserted.

Temperature Control

The nitrate monitor is intended for use in the field under ambient weather conditions. As the voltage response of the nitrate indicator electrode and fluoride reference electrode is temperature dependent, it was necessary to maintain the temperature of the solution cavity at a fixed value outside the normal range of ambient temperatures. Our method was to heat and control the temperature of the nitrate solution at 38·5 °C with an immersion heater (Pyrex, No. 33847–026) coupled with a temperature probe (Versa Therm, Model 8446), all of which are shown in Fig. 1. In order to minimise non-uniform temperatures within the solution and to ensure adequate circulation, the immersion heater was located at the centre of the solution cavity at a depth such that no appreciable direct heating of the lucite housing was encountered.

Stirring

Elimination of inhomogeneities within the solution cavity and a reproducible stirring rate were provided by the magnetic stirring bar unit indicated in Fig. 1. In order to achieve a slow, steady stirring rate, it was necessary to adapt a high-torque, slow-revolution (240 rev min^{-1}) synchronous motor to a revolving magnet removed from a commercial stirring unit. This arrangement provided adequate circulation and minimised bubble formation. These results are consistent with the flow-through unit of Milham[10] under similar conditions.

Liquid Level Control

Collection fluid in the nitrate monitor was recirculated from the flow-through unit through the LEAP sampler,[8] as indicated in Fig. 1. Briefly, a peristaltic pump within the LEAP sampler recirculates the collection fluid from the flow-through unit at 6–10 ml min^{-1} to a revolving disc adjacent to an air flow of 600 l min^{-1} within the LEAP sampler, where the solution spreads in a thin layer over the aerosol collection disc. Our laboratory tests indicated that the fluid evaporated from the disc at a rate of about 1 ml min^{-1}, depending on ambient temperature and the LEAP air flow-rate. In order to replace the evaporative losses and to maintain a constant recirculation volume, V_T, in equation (1), it was necessary to add make-up solution to the system automatically. This addition was accomplished by adapting three liquid-level sensing probes (Dyna-Sense, No. 7186–2) to the lucite housing, as indicated in Fig. 1, in such a way that the liquid level in the solution cavity was maintained between the level of two platinum probe tips. The position of the inverted-cone solution cavity below the probe level was found to provide a geometry extremely sensitive to small changes in solution volume.

Evaluation of Instrumentation and Results

A series of tests were conducted on the flow-through electrode unit in order to evaluate its performance and the results are indicated below.

Liquid Level Control

The monitor was filled with collection solution and allowed to recirculate for several minutes until the liquid-level controller triggered the addition of make-up solution. When a solenoid valve closed,[11] indicating a full volume of collection solution, the system was drained manually until the level controller was re-activated. In preliminary tests, with a rough setting of the sensing probe positions, the liquid volume was maintained to within 3 ml, limiting the error in recirculation volume (V_T plus liquid volume in tubing and sampler) to less than 5 per cent. This error could be decreased by making further adjustments. For the purpose of this nitrate measurement, it was not necessary to control the volume closely, as the collection solution was doped with fluoride ions and a fluoride-selective electrode was used as reference. However, it was necessary to re-fill the system accurately with a known volume of collection solution at the beginning of a run.

Temperature Response

The transient response of the unit to temperature changes was determined by measuring the time necessary to bring the entire stirred solution volume from room temperature to

48 °C. This measurement was accomplished by recording thermometer readings of the solution temperature after activation of the immersion heater. The results are indicated in Fig. 2. Although this test is considered to be far more severe than that anticipated under normal conditions in which only the incoming fluid need be heated, the solution volume

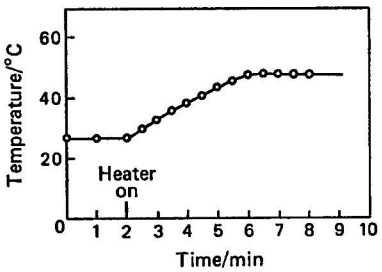

Fig. 2. Transient temperature response of flow-through unit. Flow-rate = 6 ml min^{-1}; cell volume = 44 ml; and immersion heater voltage = 40 V.

reached 48 $\pm$ 0·5 °C in about 4 min with the immersion heater operating at 40 V (about 11 W) while maintaining a flow-rate through the cell of 6 ml min^{-1}. The response time of 4 min is much shorter than the characteristic time associated with ambient temperature changes.

Electrode Response

In order to minimise the response time of the electrodes to changes in concentration within the solution cavity, the mixing characteristics of the cavity should approach that of an ideal stirred vessel in which the feed is dispersed instantaneously throughout. Thus, assuming an ideal stirred vessel of volume V through which a solution is flowing at a rate Q, one has[12]

$$[NO_3^-] = ([NO_3^-]_0 - [NO_3^-]_i)\, e^{-\frac{t}{\tau}} + [NO_3^-]_i \quad .. \quad .. \quad .. \quad (2)$$

where $[NO_3^-]_0$ is the initial nitrate concentration within the solution cavity at $t = 0$, $[NO_3^-]_i$ is the inlet nitrate concentration and $\tau = V/Q$ is the solution residence time. Moreover, if the concentration of nitrate within the vessel is measured with a nitrate indicator electrode and fluoride reference electrode operating within the Nernstian region (about 4×10^{-5}–10^{-2} M NO_3^-) where the electrode voltage response is given by

$$\Delta E = \Delta E_0 - \frac{RT}{nF} \ln \frac{[NO_3^-]}{[F^-]} \quad .. \quad .. \quad .. \quad .. \quad (3)$$

one can combine equations (2) and (3) to yield

$$\frac{\Delta E - \Delta E_0}{RT/nF} = -\ln\left[\left(\frac{[NO_3^-]_0}{[NO_3^-]_i} - 1\right) e^{-\frac{t}{\tau}} + 1\right] - \ln \frac{[NO_3^-]_i}{[F^-]} \quad .. \quad (4)$$

where ΔE is the relative potential, ΔE_0 is the standard potential, R is the gas constant, T is the absolute temperature, n is the number of electrons transferred and F is the Faraday constant.

In order to check the validity of equation (4), two tests were conducted using a gravity-fed nitrate solution to the flow-through unit. The results of both tests are shown in Fig. 3, for which the parameters of the system were as follows: $\Delta E_0 = 73$ mV; $RT/nF = 26{\cdot}9$; $T = 38{\cdot}5$ °C; $n = 1$; $[F^-] = 10^{-2}$ M; and $V = 44$ ml.

As can be seen in Fig. 3, the response of the flow-through unit conformed closely to that of a well stirred vessel. The small drift in the results relative to the theoretical results was

caused by a decrease in head above the unit as the experiment progressed.

Bubble Formation

With a cell operating temperature of 38·5 °C, it was found that small bubbles formed on the inside surfaces of the solution cavity and that these bubbles occasionally lodged in a position adjacent to the liquid membrane of the nitrate electrode, causing an unstable electrode potential. This problem has previously been reported as one of the greatest difficulties encountered in the use of flow-through cells.[9] However, we found that the use of

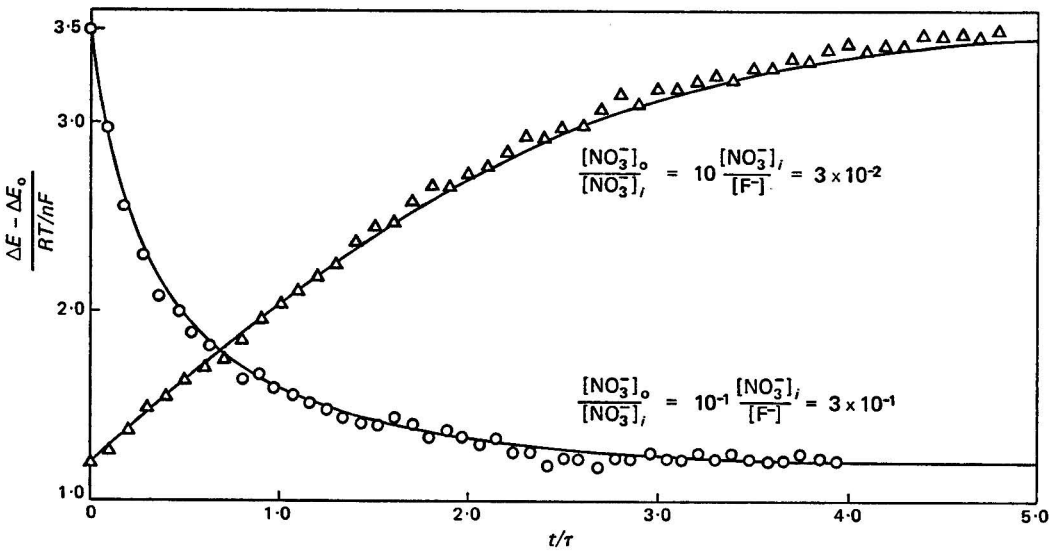

Fig. 3. Transient voltage response at flow-through unit using test parameters of Table I. Solid lines predicted by equation (4). △ indicates response with $[NO_3^-]_0 = 3 \times 10^{-3}$ M, $[NO_3^-]_f = 3 \times 10^{-4}$ M, $Q = 17{\cdot}6$ ml min^{-1}, $\tau = 2{\cdot}5$ min; ○ indicates response with $[NO_3^-]_0 = 3 \times 10^{-4}$ M, $[NO_3^-]_f = 3 \times 10^{-3}$ M, $Q = 15{\cdot}7$ ml min^{-1}, $\tau = 2{\cdot}8$ min.

a stirring rate of 240 rev min^{-1} at 38 °C normally allowed a 4-h sampling period without interference from bubbles. This problem might be eliminated either by maintaining the solution at a temperature below ambient so that gas is not desolved from the solution, or by directing a jet of fluid at the liquid membrane of the nitrate electrode. Work is currently under way to eliminate this problem.

Conclusions

The flow-through electrode unit incorporating an inverted-cone solution cavity as described in this paper provides reproducible stirring of the test solution, a constant solution temperature above ambient, a steady liquid-level recirculation volume and housing for the necessary instrumentation, while minimising the solution volume. The unit was found to behave as an ideal well stirred vessel with a time constant $\tau = V/Q$. Preliminary tests indicated that the unit is suitable for use in atmospheric nitrate particulate analysis in conjunction with a commercially available aerosol collection device.

The work described in this paper was performed by the Walden Research Division of Abcor Inc., pursuant to EPA Contract No. 68–02–0591.

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Received *May* 15*th*, 1974
Accepted *July* 22*nd*, 1974

Analyst, March, 1975, Vol. 100, pp. 163–167

The Determination of Water in Natural Gas Using a Modified Karl Fischer Titration Apparatus

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The Karl Fischer titration procedure has been extensively applied in the determination of water in solids and liquids, but not in gases. In this paper a simple method for the determination of water in natural gas by use of a modified version of a commercially available Karl Fischer titration apparatus is described.

Sample gas is passed at a known flow-rate through an involatile solvent containing a measured volume of standardised Karl Fischer reagent. Complete absorption and reaction of the water in the gas in and with the Karl Fischer reagent occurs. The time taken for complete neutralisation of the Karl Fischer reagent is measured and the water content of the gas deduced.

The procedure has been successfully applied to the analysis of gases containing from 40 to 200 v.p.m. of water with the results showing a standard deviation of 3–4 per cent. Where the composition of the gas has allowed comparisons, results agree with those obtained by gravimetric, phosphorus(V) oxide cell monitor and dew-point measurement procedures.

The distribution of natural gas is now extensive and in order to provide reserves to satisfy peak demand, natural gas is being stored in the liquid state at various plants in the United Kingdom and elsewhere.

Before liquefaction, easily condensable trace components, such as methanol, water, carbon dioxide and hydrogen sulphide, must be removed from the gas in order to avoid problems associated with blockage caused by freezing out, for example, in heat exchangers. The concentration of these constituents that can be tolerated in the raw gas and in the various sections of the cooling plant needs to be known, and a method for their accurate measurement at trace levels is highly desirable. Methods are well established for three of the substances mentioned, but not for water.

Hygrometers and other instruments, such as those based on the phosphorus(V) oxide cell, can be used for the determination of water in some gases but they are affected by condensable hydrocarbons and methanol in natural gas, so that incorrect values are obtained.

The Karl Fischer procedure for the determination of water, which is free from interference by these components, was attractive as an alternative and reference method. The technique described in this paper, using a robust, commercially available apparatus, which suits the needs of on-site analysis, facilitates the determination of water in the gas by absorption in a cell where direct reaction with Karl Fischer reagent occurs. The procedure for the determination of water in solid and liquid samples is well documented (British Standard 2511: 1970) but only a few workers have reported its application to gases.[1–3] All of these workers absorbed the water from the gas in a solvent which was predominantly methanol and used specially designed apparatus. In our application the loss of methanol from the titration cell, owing to its volatility, created procedural difficulties and consequently the much less volatile solvent mixture, ethane-1,2-diol - pyridine (4 + 1), was used; use of this solvent mixture also minimised spurious ammeter deflections, which are caused before the end-point when methanol is used.[4] In order to minimise problems associated with the decrease in strength of Karl Fischer reagent with time the more stable modified reagent proposed by Peters and Jungnickel[4] was used.

Experimental

Apparatus

Cell and titration assembly

An electrometric apparatus for Karl Fischer titrations, marketed by Baird and Tatlock (London) Ltd., was suitably modified for the determination of water in gas. The inlet tube,

designed to carry inert gas over the liquid in the titration cell, was extended, by means of a glass tube fitted with a sintered glass disc (porosity grade 1), to a point near to the bottom of the cell in order to enable gas to be bubbled efficiently through the titration solvent. The titration cell was provided with a side arm that was capped with a septum, and a wide bore drain tap was incorporated to facilitate adjustment of the level of liquid in the cell without the need to dismantle the apparatus. The cell assembly is shown in Fig. 1.

The right-hand 25-ml burette of the Baird and Tatlock apparatus was replaced by a 10-ml microburette, which was connected to the reagent reservoir containing modified Karl Fischer reagent that had a water equivalent of about 0·5 mg ml^{-1}.

Desiccant guard tubes were filled with anhydrous calcium sulphate.

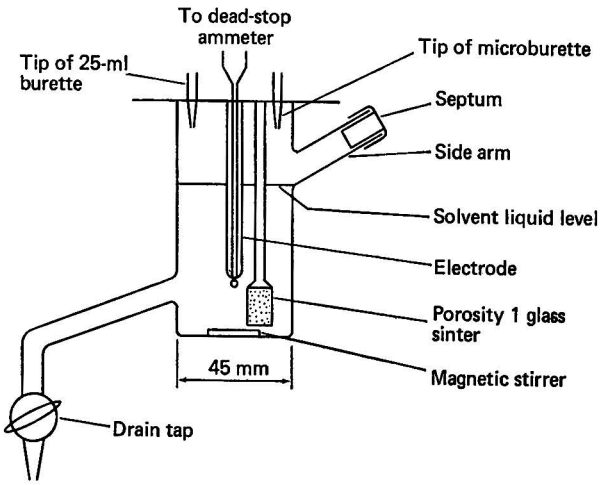

Fig. 1. Modified cell for Karl Fischer titration apparatus.

Gas sampling

The pressure of the natural gas or test gas was reduced to a gauge pressure of 14 kN m^{-2} (2 lb in^{-2}) and was passed to the gas inlet of the cell using $\frac{1}{4}$-in o.d. stainless-steel tubing, which minimised water absorption and desorption effects. The gas flow-rate through the cell was regulated by using a stainless-steel fine control valve inserted in the stainless-steel sample line.

Reagents

Karl Fischer reagent (equivalent to 5 mg ml^{-1} of water). The modified Karl Fischer reagent supplied by Hopkin and Williams Ltd. is suitable.

Pyridine. General Purpose Reagent for Karl Fischer titration (maximum water content of 0·04 per cent.) can be used.

Ethane-1,2-diol. Analytical-reagent grade.

Ethane-1,2-diol - pyridine solvent. To 800 ml of ethane-1,2-diol add 200 ml of pyridine.

Dry ethane-1,2-diol - pyridine solvent. By use of Karl Fischer reagent (equivalent to 5 mg ml^{-1} of water) determine the water content of the solvent mixture. Deduce the volume of the reagent that would be necessary to neutralise the water in 1 l of solvent, and add this volume of Karl Fischer reagent to 1 l of solvent.

Karl Fischer working reagent. To 10 ml of the Karl Fischer reagent add 90 ml of dry solvent.

1 ml of working reagent $\approx$ 0·5 mg of water.

Procedure

Standardisation of Karl Fischer reagent (water equivalent, 0·5 mg ml^{-1})

Fill one of the reservoirs of the apparatus with Karl Fischer reagent (equivalent to 5 mg ml^{-1} of water) and the other with working reagent. Fill the titration cell with the

ethane-1,2-diol - pyridine solvent to a level just below the junction of the cell and its side arm. Next, fill the burettes with the two Karl Fischer reagents, discard the contents to eliminate residual moisture in the burettes, then re-fill the burettes. Pass high purity nitrogen or dried sample gas through the cell at a flow-rate of 1 l min^{-1} to act as an electrode depolariser. Bring the ammeter to its neutral point by the addition of Karl Fischer reagent (5 mg ml^{-1}) to the cell and then re-adjust the liquid level in the cell.

Inject 2 μl of water into the cell, from a micro-syringe via the septum, and return the ammeter to its neutral position by using the Karl Fischer working reagent from the micro-burette. Repeat the determination until consecutive results duplicate satisfactorily, then calculate the water equivalent of the Karl Fischer working reagent used.

Determination of water in sample gas

Replace the dry gas with the sample gas and allow the latter to by-pass the cell and flow through a soap bubble flow meter. Adjust the sample gas flow-rate to 1 l min^{-1}. Return the gas flow through the cell for 30 min to ensure the complete elimination of dry gas from the system and record the ambient temperature and air pressure.

Next, return the ammeter to its neutral point by using Karl Fischer reagent (5 mg ml^{-1}), thus ensuring that the titration solvent is momentarily completely dry. Immediately start a stop-clock and add about 3 ml of Karl Fischer working reagent from its burette to the titration cell. Record the volume of Karl Fischer reagent added only when the burette reading becomes constant, about 10 min being allowed for the relatively viscous reagent to drain from the burette walls. Stop the clock when the ammeter indicator returns to its neutral point, in order to record the time required for the water in the timed gas flow to neutralise the Karl Fischer reagent added to the titration cell.

Calculate the water content of the sample from the results obtained.

Calculation

$$\text{Water content of gas, } Q = \frac{V \times W \times 22{\cdot}4 \times 10^3}{T \times R \times Y \times 18} \text{ v.p.m. of water}$$

where V is the volume of modified Karl Fischer reagent added to the cell (ml); W is the water equivalent of the modified Karl Fischer reagent (mg ml^{-1}); T is the time of flow of the sample gas (min); R is the sample gas flow-rate (l min^{-1}); Y is the factor to reduce volume of gas passed to standard conditions; and v.p.m. are the volume parts of water vapour per million volume parts of gas.

Results

Water Absorption Efficiency in the Titration Cell

A reliable measure of water content will be obtained only if the water in the sample gas is removed completely by the solvent and reacts immediately with the Karl Fischer reagent in the cell. The absorption efficiency of the solvent and Karl Fischer reagent in the cell was tested in two ways. The volume of 0·5 mg ml^{-1} Karl Fischer reagent added to the cell containing dried solvent was kept constant at 3 ml and the sample gas flow-rate was varied from 1 to 5 l min^{-1}. The results obtained are shown in Table I. In addition, the sample gas flow-rate was maintained constant at 4 l min^{-1} and the volume of 0·5 mg ml^{-1} Karl Fischer reagent added to the cell was varied from 1 to 5 ml [see Table II (*a*)]. A second natural gas sample was employed while maintaining the gas flow-rate at a lower value of 1 l min^{-1} [see Table II (*b*)].

The results [Tables I and II (*a*)] that refer to the same gas indicate a mean water content of 49·6 and 48·0 v.p.m. for the two techniques, which were shown not to be statistically different. It is evident, therefore, that the indicated values were independent of the time taken to carry out a determination, the volume of the sample gas and its flow-rate when this was not greater than 5 l min^{-1}. The efficiency of absorption of water by the cell liquid was inferred to be virtually 100 per cent., confirming the findings of Muroi[2] and Archer and Hilton.[3] The results in Tables II (*a*) and (*b*) show that a maximum value for the water content of the sample is obtained when the cell contains 2·5–3 ml of 0·5 mg ml^{-1} reagent. Although no explanation can be offered at present for this observation it is apparent, from

TABLE I

WATER CONTENT OF NATURAL GAS FOUND BY KARL FISCHER TITRATION

Constant Karl Fischer reagent addition, 3 ml; gas flow-rate, variable.

Gas flow-rate/l min^{-1}	Time of test/min	Water content at N.T.P., v.p.m.
1·35	41	50·2
1·35	44	46·7
2·0	29	47·8
2·0	28	50·4
2·6	22	48·1
2·6	23	45·9
3·25	17	50·1
3·25	16	53·3
4·0	14	48·8
4·0	14	50·2
4·6	12	50·2
4·6	12	50·2
5·3	11	49·6
5·3	10	53·4
	Mean ..	49·6

results of the determination of water in nitrogen mixtures, that the maximum value observed is the true water content of the sample. The experimental procedure described was based upon these findings, and involved the use of a steady flow-rate of gas (1 l min^{-1}) and the addition of 3·0 ml of 0·5 mg ml^{-1} Karl Fischer reagent.

TABLE II

WATER CONTENT OF TWO NATURAL GAS SAMPLES BY KARL FISCHER TITRATION

Gas flow-rate, constant; Karl Fischer reagent addition, variable.

	(*a*) Gas flow 4 l min^{-1}		(*b*) Gas flow 1 l min^{-1}	
Karl Fischer reagent addition/ml	Time of test/min	Water content at N.T.P., v.p.m.	Time of test/min	Water content at N.T.P., v.p.m.
1·0	4·8	46·8	10·5	74·1
1·5	—	—	15·0	77·6
2·0	9·5	49·9	19·3	80·6
2·5	11·5	51·5	23·3	83·4
3·0	14·0	49·5	28·3	82·3
3·5	17·25	46·3	33·5	80·6
4·0	19·8	46·9	44·0	68·0
4·5	—	—	52·5	65·5
5·0	26·8	45·5	—	—
	Mean ..	48·0	Mean ..	76·5

Determination of Water in Moist Nitrogen Samples

Mixtures containing water vapour in nitrogen were prepared in 5·4-l aluminium cylinders at a gauge pressure of 7000 kN m^{-2} (1000 lb in^{-2}) and were analysed by the method described, with a moisture monitor based on the technique of absorption by phosphorus(V) oxide, and by absorption in magnesium perchlorate. The results are shown in Table III. The agreement between the methods showed that the recovery of water in the gas by Karl Fischer titration was satisfactory and quantitative. The results also show that the maximum value observed previously was the true value for the water content of the sample.

TABLE III

DETERMINATION OF WATER IN NITROGEN

	Water content, v.p.m.	
Technique	Cylinder 1	Cylinder 2
Karl Fischer titration	85, 83	83, 81, 84
Moisture monitor	82	83
Magnesium perchlorate absorption	80	87

In this instance the moisture monitor provided a result more quickly, but it cannot be used with natural gas because of the presence of interfering compounds. The method

involving absorption in magnesium perchlorate is tedious and cannot be used for natural gas as methanol is also absorbed. These two methods were, however, suitable for the determination of water in nitrogen, and as reference procedures against which to compare the Karl Fischer method.

Application of the Procedure to Natural Gas

The procedure described has been used to measure the concentration of water in a natural gas during liquefaction at pilot scale and the results have been compared with those obtained by use of a UGC Dewscope hygrometer, fitted with a bubbler containing paraffin in order to remove easily condensable hydrocarbons. Values for four different samples are given in Table IV; these results show that the procedure was applied successfully to natural gas analysis.

TABLE IV

DETERMINATION OF WATER IN NATURAL GAS

	Water content at N.T.P., v.p.m.	
Sample	Karl Fischer procedure	Dewscope
1	43	48
2	72	69
3	94	89
4	49	45

Precision of the Procedure

The over-all precision of the method was evaluated from a number of determinations of the water content of a natural gas sample by using the procedure described. A mean value of 95·8 v.p.m. of water was obtained with a standard deviation of 3·2 v.p.m.

Discussion

The method was required essentially as an absolute standard against which other instrumental procedures could be checked. Water sensors relying on hygrometry and chemical cells [*e.g.*, the phosphorus(V) oxide cell] are subject to interference from trace constituents in natural gas, such as hydrocarbons and methanol, and for their successful application separation procedures prior to water determination would be required.

The Karl Fischer titration procedure is specific for water and the procedure described has been shown to be applicable to natural gas. Water contents of between 40 and 200 v.p.m. in natural gas are readily determined with a standard deviation of 3–4 per cent. It may be possible to extend the technique to other gases containing more than 200 v.p.m. of water, but this need has not yet arisen.

Conclusions

A commercially available Karl Fischer titration apparatus that is suitable for the determination of water in liquids and solids, has, after slight modification, been applied successfully to gases. The efficiency of water absorption from the gas was shown to be virtually complete and consequently a procedure for water determination in at least nitrogen and natural gas samples was established.

Results obtained on a natural gas sample containing 96 v.p.m. of water when using the procedure had a standard deviation of 3–4 per cent. The method has been successfully applied to natural gas samples containing up to 200 v.p.m. of water, but the standard deviation is greater than 3 per cent. for samples containing less than 40 v.p.m.

This paper is published by permission of British Gas. The author also thanks K. R. Compson (present address: AEI, Scientific Apparatus, 1 Dock Road, Urmston, Manchester) for assistance with the experimental work.

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Received *June 24th*, 1974
Accepted *October 30th*, 1974

Analyst, March, 1975, Vol. 100, pp. 168–172

A Simple Reaction-rate Method for the Determination of Biuret

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The phenol - hypochlorite reaction is employed for the determination of biuret in aqueous solutions. The recommended reaction-rate method is fast, simple, sensitive (0·018 A min^{-1} per micromole of biuret), accurate (to 2 per cent.) and precise (3 per cent. relative standard deviation). The useful analytical range of concentrations of biuret is $1·6 \times 10^{-5}$ to $1·3 \times 10^{-3}$ M. The effect of the phenol concentration on the reaction rate has been studied.

The effect of interfering species such as ammonium chloride, urea and cyanurate has also been investigated.

It is known that ammonia and urea react with hypochlorite and phenol to give coloured indophenols.[1–3] Mechanisms of the above reactions have been proposed by various investigators,[2,4] and the kinetics as well as the analytical data have been given in the literature.[5–7] We have investigated the urea - hypochlorite - phenol reaction both in acidic and alkaline solutions,[6–8] and, in addition, have found that many organic substances that react with hypochlorite to give chloramine (NH_2Cl) also yield coloured indophenols in the presence of phenol, the colours given depending on the pH of the reaction system. Thiourea, formamide and biuret give the same reaction, with the formation of an intermediate yellow product that absorbs light at 465 nm. With biuret the reaction takes place in alkaline solutions and the yellow product is slowly converted into a final bluish-green indophenol, which is characterised by its absorption bands at 640 and 355 nm.

The various steps of the reaction are as follows: the formation of (1) chloramine from biuret and hypochlorite ions, (2) quinone chloroimine from the chloramine and phenol and (3) the final indophenol product with the excess of phenol.

The formation of an intermediate quinone chloroimine gains support from the fact that the same phenolindophenol is obtained by allowing *p*-aminophenol to react with hypochlorite first, and then adding phenol to the mixture.

When the same reaction takes place in acidic solution no product absorbing at 640 nm is obtained, although the yellow intermediate compound appears as with alkaline solutions. On standing, the colour of this product changes from yellow to light pink; a similar effect is observed when the solution of the bluish green indophenol is acidified.

Experimental

Apparatus

The investigations reported in this work were performed with a modified Heath 701 single-beam spectrophotometer. The modification consists in replacing the original cell-basket and its support with a home-made cuvette placed in a double-walled brass housing, which is connected to a Sargent heater and circulator equipped with a temperature monitoring unit. The brass housing of the cuvette is mounted on a magnetic stirrer, a plastic plate with a magnetic rotor inside, which is powered by tap water, compressed air or a vacuum (G. F. Smith Chemical Co., Columbus, Ohio, U.S.A.).

The observation cell is a Vycor-glass tube, 8·3 cm long, with a flat bottom. The internal and external diameters of this cuvette are 1·53 and 1·8 cm, respectively. The photocurrent from the photomultiplier output is fed to the log - lin unit attached to a chart recorder (Heath EU–20–28). Depending on the setting on the log - lin module, the time course of the absorbance or transmittance of the reacting system can be recorded.

Reagents

All reagents were of analytical-reagent grade and were used as supplied.

Biuret solutions. All the solutions of biuret were prepared from an aqueous stock solution ($1{\cdot}67 \times 10^{-2}$ M) by dilution with a borate - sodium hydroxide buffer (pH 10).

Phenol solutions. All the phenol solutions employed for the experiments were prepared from an 8·0 per cent. aqueous solution of phenol (0·851 M) by dilution with double-distilled water.

Hypochlorite solutions. The hypochlorite reagent used was Klinex bleach liquid (a locally prepared commercial sodium hypochlorite solution, with pH 12), with an original concentration of free chlorine of about 5 per cent.

Spectral Study

For the spectral study the following procedure was followed: 20 ml of a $1{\cdot}67 \times 10^{-4}$ M solution of biuret in a buffer of pH 10 were mixed with 0·5 ml of bleach liquid (1·38 M in hypochlorite ions) in a beaker with stirring. The mixture was left to react for 30 s and then 10·0 ml of a $4{\cdot}25 \times 10^{-2}$ M aqueous solution of phenol were added. Immediately after mixing, an aliquot of the final mixture was placed in a 1-cm quartz cuvette and its absorption spectrum was recorded with a double-beam spectrophotometer (Beckman DK), against water, at different times after the addition of the phenol. The first spectrum (shown in Fig. 1) was taken 1 min after the addition of the phenol.

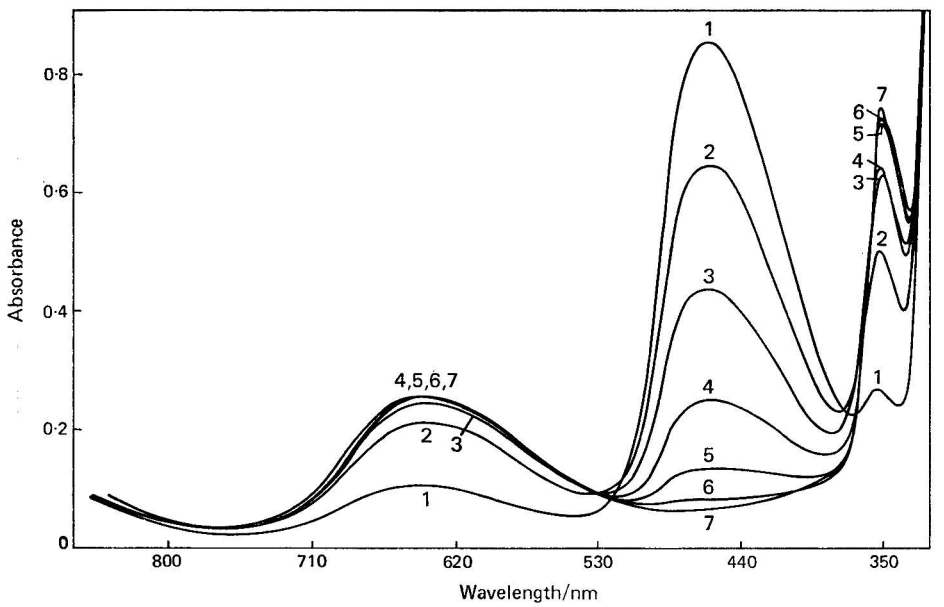

Fig. 1. Absorption spectra of reaction system biuret - hypochlorite - phenol at different times after the addition of the phenol reagent. Curves: 1, 1 min; 2, 9 min; 3, 19 min; 4, 34 min; 5, 55 min; 6, 79 min; and 7, 120 min.

Initially, the 465-nm band predominates over the bands at 355 and 640 nm. A kinetic study of the reaction system showed that the 465-nm band is due to a yellow intermediate product, and that the bands at 355 and 640 nm are attributable to the same species, *i.e.*, the bluish green indophenol formed as the final product of the reaction (the results of these experiments will be published elsewhere).

Analytical Application

For the determination of biuret in aqueous solutions by means of the above reaction, the following procedure is recommended: switch on the instrument and the electronics at least

30 min before taking any measurements. Set the wavelength at 465 nm on the monochromator and calibrate the spectrophotometer for zero absorbance with the cuvette filled with distilled water. For optimisation of the instrument variables reference should be made to the appropriate instruction manual.

Measurement of Standards

Because of the absence of a blank value and the good precision of the method, the analytical curve can easily be constructed with only two or three different standards in the range of the unknowns; 4 ml of the buffered standard solution of biuret (pH 10) were pipetted into the observation cell and then 100 μl of the hypochlorite reagent (1·38 M) were added, while stirring, with a Hamilton syringe. After an interval of 30 s, 2·0 ml of the phenol reagent ($4{\cdot}25 \times 10^{-2}$ M in phenol) were added with a 2-ml hypodermic syringe.

Two seconds after the addition of the phenol reagent the reaction can be followed by recording against time the absorbance of the reaction system.

Fig. 2 shows the curves obtained for three different concentrations of biuret. In each instance, the initial reaction rate is calculated graphically. The slope of the linear portion of the curve at the beginning of the reaction, expressed in absorbance units (A) per minute, is taken as the initial reaction rate. By plotting this value against the concentration of biuret, a straight line is obtained with a slope of 0·018 A min^{-1} per micromole of biuret. Fig. 3 shows such a graph, which is linear in the concentration range $1{\cdot}6 \times 10^{-5}$ to $1{\cdot}3 \times 10^{-3}$ M of biuret.

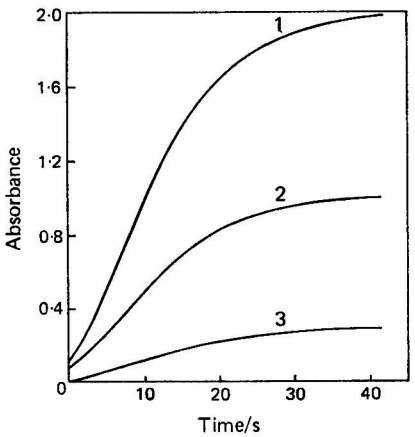

Fig. 2. Reaction curves (absorbance *versus* time at λ = 465 nm). The reaction mixture contained NaOCl at $2{\cdot}3 \times 10^{-2}$ M; phenol at $1{\cdot}4 \times 10^{-2}$ M; and biuret: 1, at $3{\cdot}32 \times 10^{-4}$ M; 2, at $1{\cdot}67 \times 10^{-4}$ M; and 3, at $4{\cdot}98 \times 10^{-5}$ M concentration.

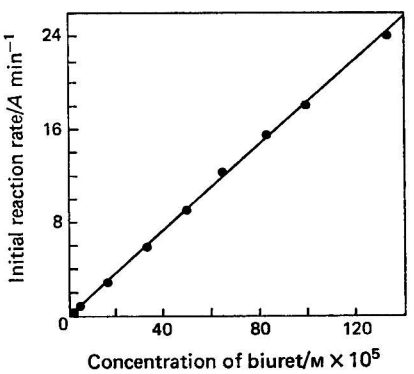

Fig. 3. Working graph for biuret determination.

Effect of Phenol Concentration on the Reaction Rate

The above experimental procedure was applied in order to study the effect of the concentration of phenol on the reaction rate. The final concentrations of biuret and hypochlorite in the reaction mixture were kept constant at $2{\cdot}180 \times 10^{-4}$ and $2{\cdot}300 \times 10^{-2}$ M, respectively, and the concentration of phenol reagent was varied from $2{\cdot}125 \times 10^{-2}$ M to $19{\cdot}125 \times 10^{-2}$ M (final concentration in the mixture $0{\cdot}70 \times 10^{-2}$ to $6{\cdot}30 \times 10^{-2}$ M). The initial reaction rate, expressed in A min^{-1}, has been determined for different concentrations of phenol and the results obtained are illustrated in Fig. 4.

The maximum reaction rate occurs at a concentration of about $4{\cdot}0 \times 10^{-2}$ M, which corresponds to a final concentration of $1{\cdot}3 \times 10^{-2}$ M of phenol in the reaction system. The ratio of the concentration of hypochlorite to that of phenol is then about 2. The decrease in the initial reaction rate for ratios of hypochlorite to phenol of less than 2 is due to the formation of trichlorophenols in addition to mono- and dichlorophenols, which are formed when this ratio is below 2. Phenol that is substituted in the *para*-position cannot react with biuret according

to the above scheme. The original phenol concentration of $4{\cdot}25 \times 10^{-2}$ M (0·4 per cent. of phenol) was selected for our experiments because it gives nearly the maximum initial reaction rate for the concentration of hypochlorite employed, and thus ensures maximum sensitivity.

Interference Study

As stated above, many compounds that react with hypochlorite to form chloramine give the same final product with phenol. Unfortunately, the rates of reaction of different species such as urea, ammonium salts and cyanurates, which commonly occur in admixtures with biuret, do not differ sufficiently to enable multi-component analysis to be attempted by a differential rate method. By applying the procedure described above, we studied the interference effect of ammonium chloride, urea and cyanurate on the reaction rate. The results for two starting concentrations of biuret are presented in Fig. 5. The ratio of the concentration of interfering species to the concentration of biuret (C_{int}/C_b) was varied from 0 to 10. The effect of ammonium salts does not seem to be significant for C_{int}/C_b ratios of up to 3 with low concentrations of biuret and for higher ratios the effect is negative, probably due to the much faster rate of formation of chloramine from ammonia, which is available initially in the reaction mixture. During the waiting time of 30 s the chloramine decomposes[9] and has no effect on the reaction rate. Cyanurates form chloramine with hypochlorite at a slower rate than NH_3 and at a faster rate than biuret. Both ammonium chloride and cyanurates consume hypochlorite ions to give chloramine or other unspecified products, which, during the 30-s waiting time, partially or completely decompose, depending on their starting concentrations. At higher concentrations these compounds drastically decrease the available concentration of hypochlorite ions, thus decreasing the rate of formation of chloramine from biuret, which is shown in Fig. 5, by the negative effect that they have on the reaction rate when the ratio C_{int}/C_b or the absolute values for their concentrations are high.

The rate of consumption of hypochlorite from urea is comparable with that from biuret and consequently the effect of urea on the reaction rate is positive.

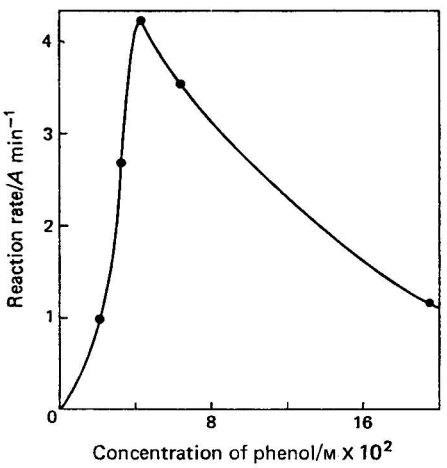

Fig. 4. Effect of phenol concentration on the reaction rate.

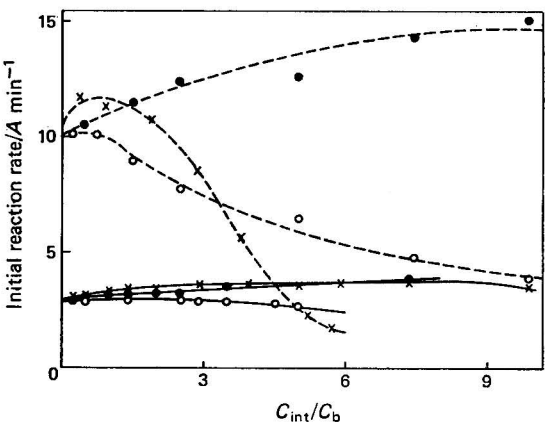

Fig. 5. Interference effect of urea (●), cyanurate (×) and NH_4Cl (○) on the reaction rate. Concentration of biuret: ———, $0{\cdot}98 \times 10^{-4}$ M and – – –, $3{\cdot}32 \times 10^{-4}$ M.

Discussion

As shown in Fig. 3, the dependence of the initial reaction rate on the concentration of biuret is linear, with a useful analytical concentration range from $1{\cdot}6 \times 10^{-5}$ to $1{\cdot}3 \times 10^{-3}$ M. The slope of the straight line is 0·018 A min^{-1} per micromole of biuret, thus indicating that the above method is very sensitive and that it can be used for the determination of biuret in aqueous solutions. The precision of the method, measured for a standard sample in the above concentration range, is shown by the 3 per cent. relative standard deviation ($n = 7$, 95 per cent. confidence level). The accuracy, calculated from the results given in Table I, was

found to be about 2 per cent. The method is very simple and any recording spectrophotometer can be used following a minor modification to the cell compartment. The time for one determination is 3 to 5 min, including the time required for calculating the slope of the recorded curve. In the absence of a blank value, the working curve can be constructed with only two or three points. All measurements reported in this work were performed at 25·0 ± 0·1 °C.

The activation energy for the reaction, as calculated from Arrhenius graphs (log $K_{obs.}$ *versus* $1/T$), was found to be 26·7 kcal. Because this value is relatively high, good thermal stabilisation of the observation cell is necessary.

The standard solutions of biuret are stable for more than 2 weeks in aqueous solution, as well as in buffered solutions of pH 10, and consequently there is no need to prepare fresh standards.

TABLE I

RESULTS FOR AQUEOUS BIURET SOLUTIONS

Concentration of biuret/M × 10^5*			
Taken	Found	Error, per cent.	Initial reaction rate/A min^{-1}
1·09	1·10	0·9	0·27
3·27	3·30	0·9	0·80
10·90	10·40	4·5	2·80
21·80	21·30	2·3	5·85
32·70	32·80	0·3	9·07
43·60	44·70	2·5	12·32
54·60	56·10	3·0	15·52
65·40	65·50	0·2	18·08
87·20	86·90	0·3	24·00
	Mean ..	1·7	

* The concentrations given are those in the reaction mixture.

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Received *April 22nd*, 1974
Accepted *July 16th*, 1974

Determination of Biphenyl and 2-Phenylphenol in Citrus Fruits by Gas - Liquid Chromatography

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Biphenyl and 2-phenylphenol are steam distilled from a citrus fruit homogenate into two portions of cyclohexane. An aliquot of the first extract is analysed for biphenyl by gas - liquid chromatography. Aliquots of the first and second extracts are combined and then cleaned up and concentrated by means of further extractions prior to the gas - liquid chromatographic determination of 2-phenylphenol.

Post-harvest treatment of citrus fruit with 2-phenylphenol and the maintenance of a certain biphenyl concentration in the air around the fruit (by, for instance, using wrappings impregnated with biphenyl) prevent the growth of moulds on the skin of the fruit during transport and storage.

Several spectrophotometric methods (with ultraviolet or visible light) have been described for the determination in citrus fruit of both biphenyl[1–3] and 2-phenylphenol.[2,4–6] Gas - liquid chromatographic methods have also been applied.[4,7–9] In most of these methods the fungicides are separated from the fruit by steam distillation before their extraction with an organic solvent. The distillation is omitted from some methods. A clean-up of the extract is always performed before the spectrophotometric determination and sometimes before the application of gas - liquid chromatography.

Fig. 1. Gas chromatograms of orange extracts. (*a*), No biphenyl added; (*b*), 20 mg of biphenyl added per kilogram of fruit.

Since 1969, a method for the determination of biphenyl in citrus fruits by steam distillation into cyclohexane and subsequent spectrophotometry of the purified extract[3,10] has been used in our laboratory, in combination with a simple gas - liquid chromatographic determination of biphenyl on the dried, crude extract from the same steam distillation[11,12] (Fig. 1). The values obtained by the spectrophotometric determinations were approximately 102 per cent. of those

values obtained with the gas - liquid chromatographic procedure described below, with a standard deviation of 3·6 per cent. for 109 samples. By using the gas - liquid chromatographic method the recovery of biphenyl added to citrus fruits (40·0–100·0 mg kg^{-1}) was 97 per cent. (standard deviation 2 per cent.; four samples). The limit of detection of biphenyl when 1 μl of the extract is chromatographed is 1 mg kg^{-1}.

For several years, we have used the spectrophotometric method of the Nordic Committee on Food Analysis[5] for the determination of 2-phenylphenol. Although the 2-phenylphenol in the cyclohexane extract obtained after steam distillation is cleaned up and a colour reaction is performed, the natural compounds extracted from the citrus fruits often contribute to the light absorption, with the result that the 2-phenylphenol values found are slightly higher than the actual levels. Such interference was also observed by other authors using other methods.[2,4,6,9] In order to avoid this interference, a method involving a clean-up step followed by a gas - liquid chromatographic determination of 2-phenylphenol has now been elaborated. The 2-phenylphenol is extracted with small volumes of 1 N sodium hydroxide solution from the cyclohexane extract obtained in the application of the Nordic Committee on Food Analysis method,[5] the alkaline extract is acidified, and the 2-phenylphenol is re-extracted into a small volume of cyclohexane. The volume of cyclohexane in which the 2-phenylphenol is contained is thus decreased ten-fold in order to increase the sensitivity of the method.

Fig. 2 shows the great difference between the gas chromatograms obtained from the cyclohexane extract of the distillate of lemon after ten-fold concentration (*a*), by evaporating the solvent and (*b*), by using the clean-up procedure described here. Fig. 3 shows chromatograms of cleaned up orange extracts. The chromatograms in Figs. 2 and 3 should be compared with the chromatograms published by Beernaert,[9] in which interferences from plant co-extractives with the same retention time as 2-phenylphenol are observed.

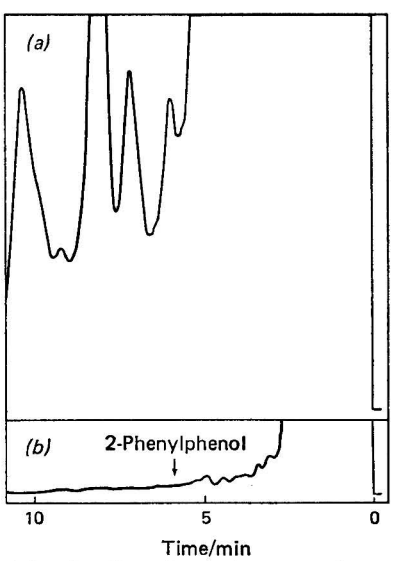

Fig. 2. Gas chromatograms of combined, dried cyclohexane extracts obtained from steam distillation of a lemon sample. The combined extracts were concentrated ten-fold by (*a*), evaporation of the solvent before injection and (*b*), the clean-up procedure.

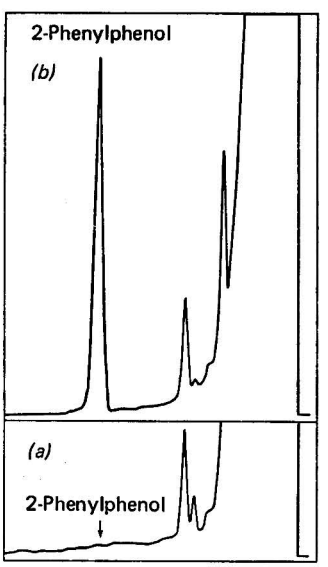

Fig. 3. Gas chromatograms of orange extracts. (*a*), No 2-phenylphenol added; (*b*), 4 mg of 2-phenylphenol added per kilogram of fruit.

The efficiency of the clean-up procedure has been examined in analyses of 31 samples of citrus fruits, selected because of their low 2-phenylphenol content. Table I shows the amount of 2-phenylphenol found in orange, lemon and grapefruit using the spectrophotometric[5] and the gas - liquid chromatographic methods. The spectrophotometric method gave results which were 0·2–1·5 (average 0·9) mg kg^{-1} higher than the results obtained with the gas -

liquid chromatographic method. In many of these samples no absorption maximum was observed at the expected wavelength, which indicates that the spectrophotometric results were incorrect.

The low levels of 2-phenylphenol shown by gas - liquid chromatography (Table I) were not artifacts. This was verified both qualitatively and quantitatively by using thin-layer chromatography,[13] which was performed both with and without the colour reaction on the cleaned up sample extracts and on 2-phenylphenol standards. When the colour reaction was omitted, the 2-phenylphenol area of the chromatogram of the sample was extracted by shaking with 1 N hydrochloric acid and cyclohexane. The dried cyclohexane extract was injected into the gas chromatograph before and after silylation with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide. The R_F value for the compound extracted from the fruit was identical with the R_F value for the 2-phenylphenol standard and the retention times for the original and silylated compound from the fruit were identical with the corresponding figures for the original and silylated 2-phenylphenol. The 2-phenylphenol concentration levels found were in all instances in good agreement with the levels obtained when determinations were carried out as described under Procedure (Table I).

TABLE I

COMPARISON OF CONCENTRATIONS OF 2-PHENYLPHENOL FOUND IN CITRUS FRUIT BY USING THE GAS - LIQUID CHROMATOGRAPHIC METHOD AND A SPECTROPHOTOMETRIC METHOD[5]

	Concentration of 2-phenylphenol/mg kg^{-1}	
Sample	Gas - liquid chromatography	Spectrophotometry
Orange	0·6	1·3
	0·2	1·0*
	0	0·8*
	0·1	1·0*
	0·4	1·4*
	0·8	1·9*
	0	1·3*
	0	0·8*
	0	1·4*
	0	1·3*
	0·07	1·6*
	0·05	1·2*
	0·06	1·1*
	0	1·2*
	0·07	1·4*
	0	1·1*
	0	1·2*
	0	1·0*
	0·08	0·5*
Lemon	1·0	1·2
	0	1·4
	0·3	1·2*
	0	1·1
	0·1	1·4
	0·8	1·4
Grapefruit	0·05	0·7*
	0·2	0·8*
	0·06	0·7*
	0·5	1·2*
	0·4	1·0
	1·1	1·7

* No absorption maximum was observed.

The recovery, by using the steam distillation process,[5] of 2-phenylphenol added to citrus fruits was 90–100 per cent. When 0·160–0·960 mg of 2-phenylphenol was taken through the above clean-up steps, 99 per cent. (standard deviation 2 per cent.; 4 samples) was recovered. When 2-phenylphenol was added to citrus fruits (4·00–10·00 mg kg^{-1}) and taken through the whole procedure, the recovery was 94 per cent. (standard deviation 3 per cent.; 4 samples).

The limit of detection of 2-phenylphenol when 1 μl of the final extract is chromatographed is 0·1 mg kg^{-1} (*cf.*, the limit of 5 mg kg^{-1} for the procedure described by Morries[8]).

Method

Apparatus

Mincer. With 4-mm holes in grinding plate.
Waring blender.
Heating mantle. Capacity for 2-l flask; with rheostat control, 500 to 550 W.
Clevenger trap. Modified, see Fig. 1, reference 3.
Gas chromatograph with flame-ionisation detector.
Column for biphenyl determination. Glass column (5 ft × $\frac{1}{8}$ in) with 5 per cent. Carbowax 20M on Chromosorb W, AW-DMCS, 60–80 mesh. Gas flow-rates: nitrogen, about 25 ml min^{-1}; hydrogen, about 30 ml min^{-1}; and air, about 280 ml min^{-1}. Column temperature, 155–160 °C. Retention time, about 4 min.
Column for 2-phenylphenol determination. Glass column (6 ft × $\frac{1}{8}$ in) with a mixture (1 + 1) of 10 per cent. DC 200 and 15 per cent. QF1 on Chromosorb W, AW-DMCS, HP, 80–100 mesh. Gas flow-rates: nitrogen, about 35 ml min^{-1}; hydrogen, about 30 ml min^{-1}; and air, about 280 ml min^{-1}. Column temperature, 180 °C. Retention time, about 6 min.

Reagents

All reagents must be of analytical-reagent grade.
Sulphuric acid, concentrated.
Antifoam agent. Dow Corning Antifoam A.
Cyclohexane.
Sodium sulphate, anhydrous.
Sodium hydroxide solution, 1·0 N.
Hydrochloric acid, 6·0 N.
Standard solutions of biphenyl. (*a*) Stock solution. Dissolve 100·0 mg of biphenyl in cyclohexane and make up to 100·0 ml. (*b*) Dilute the stock solution so as to obtain standard solutions containing 10·00–800 μg ml^{-1} of biphenyl.
Standard solutions of 2-phenylphenol. (*a*) Stock solution. Dissolve 100·0 mg of 2-phenylphenol in cyclohexane and make up to 100·0 ml. (*b*) Dilute the stock solution so as to obtain standard solutions containing 5·00–300 μg ml^{-1} of 2-phenylphenol.

Procedure

Prepare the first extract in the manner described under Procedure in reference 3.
Reconnect the Clevenger trap, introduce 20 ml of water and 40 ml of cyclohexane into it and prepare the second extract in exactly the same way.

Determination of biphenyl

In order to determine the biphenyl content of the extract, inject a 1-μl aliquot of the first cyclohexane extract and a 1-μl volume of a standard solution with about the same biphenyl concentration into the gas chromatograph and compare the peak heights. (The standard graph is a straight line passing through the origin in the concentration range 0–1000 μg ml^{-1} of biphenyl.)

Determination of 2-phenylphenol

Shake a mixture of 20·0 ml of each of the two 50·0-ml cyclohexane extracts and 5·0 ml of 1 N sodium hydroxide solution in a separating funnel for 3 min. Separate and centrifuge the turbid, alkaline phase. Transfer the clear alkaline extract so obtained into another separating funnel with a pipette, and add the cyclohexane phase from the centrifuge tube to the remaining cyclohexane phase in the original separating funnel. Re-extract the cyclohexane solution with two 5·0-ml volumes of sodium hydroxide solution. Acidify the combined alkaline phases with 6·0 ml of 6 N hydrochloric acid. Add 4·00 ml of cyclohexane and shake for 3 min, separate the layers and dry the cyclohexane extract with anhydrous sodium

sulphate. Inject a 1-μl aliquot of the dried extract and a 1-μl volume of a standard solution with about the same 2-phenylphenol concentration into the gas chromatograph and compare the heights of the peaks obtained. (The standard graph is a straight line passing through the origin in the concentration range 0–300 μg ml^{-1} of 2-phenylphenol.)

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Received *June 17th*, 1974
Accepted *October 8th*, 1974

Spectrophotometric Determination of Thiambutosine

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N-(4-Butoxyphenyl)-*N'*-(4-dimethylaminophenyl)thiourea (thiambutosine) is made to react with 2,3-dichloro-1,4-naphthoquinone in an ethanolic medium and on rendering the reaction mixture alkaline with ethanolic ammonia solution a purple colour is developed with an absorption maximum at 540 nm. A procedure based on this reaction is described for the assay of thiambutosine in micro-amounts. The method is applied to its determination in tablets. The results are in agreement with those obtained by the official method.

In continuation of the previous work,[1,2] a spectrophotometric method is described for the determination of thiambutosine, a well known anti-leprosy drug. Various procedures for its determination include non-aqueous titrimetric[3] and spectrophotometric[3,4] methods. Both of these methods are non-specific for the thiourea moiety in the drug. In view of the sensitivity and specificity of the reaction between thiourea and 2,3-dichloro-1,4-naphthoquinone,[1,2] it was thought to be of interest to employ this reagent in the spectrophotometric determination of thiambutosine.

In the present work, suitable reaction conditions were established. The procedure is applied successfully to the assay of thiambutosine in pure samples and in tablets containing it. The results compare favourably with those obtained by the official procedure.

Experimental

Apparatus

All spectral measurements were carried out on a Spectronic 20 spectrophotometer (Bausch & Lomb) equipped with four matched 10-ml cells that have a 1-cm light path.

Reagents

Thiambutosine B.P., absolute ethanol (Indian Pharmacopoeia) and copper acetate (Riedel de Haen) were used. Ethanolic ammonia solution (2·5 per cent. *m/V*) and 2,3-dichloro-1,4-naphthoquinone reagent solution (0·026 per cent. *m/V*) were prepared as described previously. All other reagents were of analytical-reagent grade.

Standard solution of thiambutosine, 0·05 *per cent.* m/V, *in absolute ethanol.*

Procedure

Determination of Thiambutosine

A standard solution containing 0·5 to 2·0 mg of thiambutosine was mixed with 3·0 ml of ethanolic ammonia solution and 12·0 ml of 2,3-dichloro-1,4-naphthoquinone reagent solution in a 25-ml calibrated flask. The final volume was adjusted to the mark with absolute ethanol and the reaction mixture was allowed to stand for 10 min at room temperature. The absorbance was measured at 540 nm against the blank.

The blank consisted of 12·0 ml of 2,3-dichloro-1,4-naphthoquinone reagent solution plus 3·0 ml of ethanolic ammonia solution diluted to 25 ml with absolute ethanol.

Determination of Thiambutosine in Tablets

Twenty tablets were weighed and powdered. An aliquot of the powder equivalent to 50 mg of thiambutosine was weighed accurately. Four equal portions of hot ethanol (20·0 ml) were used to extract thiambutosine from the powder. Each time, the extracts were filtered through Whatman No. 40 filter-paper. The residue on the filter-paper was then washed with 10·0 ml of warm ethanol. The filtrate and the washings were combined in a 100-ml calibrated flask and, after cooling, the volume was adjusted to the mark with the solvent. The solution was analysed by the above procedure.

Factors that Affect the Reaction of Thiambutosine with 2,3-Dichloro-1,4-naphthoquinone Reagent

Concentration of 2,3-Dichloro-1,4-naphthoquinone Reagent

The absorbance at 540 nm of the coloured product formed by the reaction of thiambutosine with 2,3-dichloro-1,4-naphthoquinone increased as the concentration of the reagent increased. The maximum absorbance was obtained in the presence of 12·0 ml of the reagent solution and decreased slightly on further increase in the volume of reagent solution (Fig. 1).

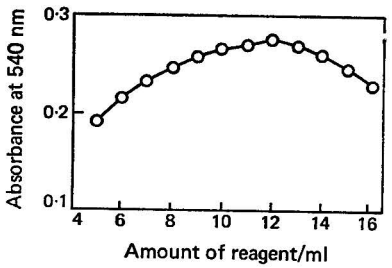

Fig. 1. Effect of the concentration of 2,3-dichloro-1,4-naphthoquinone reagent solution in a 25·0-ml reaction mixture on the absorption at 540 nm of the product formed on reaction with 1·5 mg of thiambutosine when using 3·0 ml of ethanolic ammonia solution.

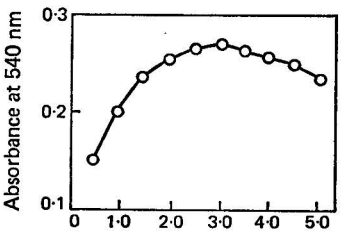

Fig. 2. Effect of the concentration of ethanolic ammonia solution in a 25·0-ml reaction mixture on the absorption at 540 nm of the product formed on reaction of 1·5 mg of thiambutosine with 12·0 ml of the reagent solution.

Concentration of Ammonia

The typical purple colour developed after the reaction of the ethanolic ammonia solution with the thiambutosine and the 2,3-dichloro-1,4-naphthoquinone reagent. Maximum colour intensity was obtained in the presence of 3·0 ml of ethanolic ammonia solution (Fig. 2).

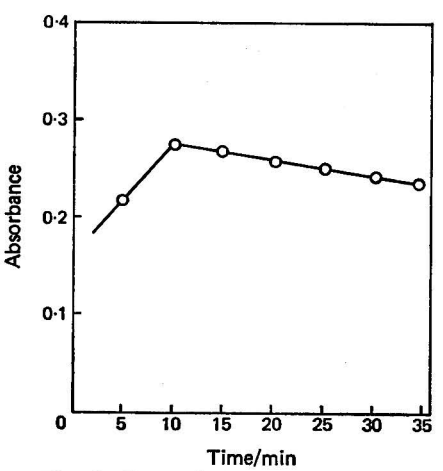

Fig. 3. Rate of development of purple coloration after reaction of 1·5 mg of thiambutosine with 12·0 ml of reagent solution when using 3·0 ml of ethanolic ammonia solution in a total reaction volume of 25·0 ml.

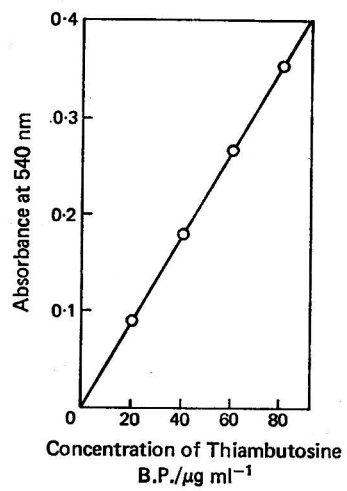

Fig. 4. Effect of the amount of thiambutosine in a 25·0-ml reaction mixture on the absorption at 540 nm of the product formed on reaction with 12·0 ml of the reagent solution when using 3·0 ml of ethanolic ammonia solution.

Time of Reaction

Maximum colour intensity developed on keeping the reaction mixture for 10 min at room temperature, and then decreased slightly on further standing (Fig. 3).

Concentration of Thiambutosine

The absorbance at 540 nm was proportional to the amount of thiambutosine in the range 20–80 μg per millilitre of reaction mixture (Fig. 4).

Results and Discussion

Thiambutosine was made to react with 2,3-dichloro-1,4-naphthoquinone in the presence of ammonia to give a typical purple-coloured product with an absorption maximum at 540 nm (Fig. 5).

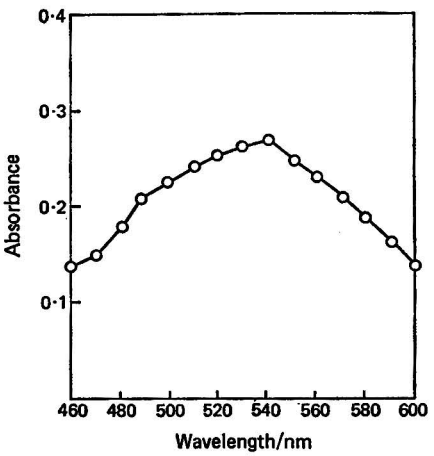

Fig. 5. The absorption spectrum of the product of the reaction between 1·5 mg of thiambutosine and 12·0 ml of the reagent solution when using 3·0 ml of ethanolic ammonia solution in a total reaction volume of 25·0 ml.

Samples of thiambutosine were obtained from commercial sources and analysed by the proposed as well as the official procedures. The percentage recovery and the standard deviation calculated from a series of experiments are given in Table I.

TABLE I

DETERMINATION OF THIAMBUTOSINE IN SAMPLES

Sample No.	Recovery, per cent., obtained by— official method	proposed method
1	99·63 ± 0·485*	99·98 ± 0·473*
2	99·80 ± 0·487	99·75 ± 0·471

* Standard deviation calculated from ten determinations.

The proposed procedure was also applied to the analysis of thiambutosine tablets. The results are in good agreement with those obtained by the official method (Table II). The usual

TABLE II

DETERMINATION OF THIAMBUTOSINE IN TABLETS

Sample No.	Labelled amount per tablet/mg	Recovery per tablet obtained by— official method/mg	proposed method/mg
1	500	499·23 ± 1·269*	500·37 ± 2·077*
2	500	499·25 ± 0·8299	499·37 ± 0·7864

* Standard deviation calculated from ten determinations.

tablet diluents, lubricants and excipients do not interfere in the analysis by the proposed method (Table III). The method is simple, rapid and accurate.

TABLE III

RECOVERY OF THIAMBUTOSINE FROM VARIOUS EXCIPIENTS BY THE PROPOSED METHOD

Sample	Excipient	Recovery, per cent.*
25 mg of thiambutosine: 200 mg of excipient	Stearic acid	100·45
	Magnesium stearate	100·47
	Calcium sulphate	100·38
	Talc	100·78
	Sucrose and maize starch	100·69
25 mg of thiambutosine: 10 g of excipient	Citric acid	99·84
	Potassium hydrogen carbonate	99·95
	Potassium hydrogen carbonate, citric acid and sucrose (1 + 1 + 1)	99·70

* Average recovery of three experiments.

Conclusion

Suitable reaction conditions have been established for the assay of thiambutosine in the range 20 to 80 μg per millilitre of reaction mixture. The method is rapid, has a reproducibility of ±0·473 per cent. and the results compare favourably with those obtained by the official method.

The authors express their sincere thanks to Dr. C. S. Shah, Principal, L.M. College of Pharmacy, Ahmedabad-9, India, for providing the facilities to carry out this work.

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Received *May 2nd*, 1974
Accepted *July 22nd*, 1974

Spectrophotometric Determination of Vanadium in Steels with *o*-Phenylenediamine

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A simple method for the spectrophotometric determination of vanadium is described. The absorbance of the yellow colour obtained with vanadium(V) and *o*-phenylenediamine in the presence of acetic acid is measured at a wavelength of 400 nm between pH 2·5 and 3·2 and is found to obey Beer's law between concentrations of 0·5 and 10 p.p.m. of vanadium. The effect of iron, up to a level of 200 p.p.m., can be masked with fluoride ions. For steels containing less than 1 per cent. of vanadium a prior separation of iron, either by extraction into diethyl ether or by electrolysis at a mercury cathode, is advantageous. The method is found to be suitable for the determination of vanadium in high-speed steels and chromium - vanadium steels.

Vanadium, an important addition to certain types of alloy steels and high-temperature alloys, is generally determined by use of a titrimetric method when present in high concentrations. When the percentage is relatively low, the vanadium content is generally determined colorimetrically with hydrogen peroxide or as tungstovanadophosphate[1] or molybdovanadophosphate.[2] Titanium interferes in the hydrogen peroxide method; moreover, a large excess of hydrogen peroxide changes the colour of the solution from red - brown to yellow and reduces the colour intensity.

The tungstovanadophosphate method is selective and fairly sensitive, but that method requires the molar ratio of phosphoric acid to sodium tungstate to be in the range 3:1–20:1 and the tungstate concentration in the sample to be 0·01–0·1 M. Molybdenum(V) also gives a yellow colour with the reagent.

In recent years, several organic reagents have received much attention. These include hydroxylammonium derivatives,[3,4] hydroxamic acids,[5,6] bromothioxamic acid[7] and acetoacetanilide[8]; chromogenic reagents, such as Nevarol NS,[9] have also been suggested. *o*-Phenylenediamine hydrochloride was first used by Rosenthaler[10] for the detection of vanadates. It has been observed that the free base *o*-phenylenediamine can be utilised for the spectrophotometric determination of vanadium in steels. However, in the presence of mineral acids the colour changes to orange and the sensitivity is reduced.

Experimental

Wavelength and Absorbance

The absorption spectrum of a 4 p.p.m. solution of vanadium was recorded in the absorbance range 350–500 nm. The complex exhibits an absorbance maximum at a wavelength of 400 nm, so this wavelength was chosen for all measurements.

Effect of pH

The dependence of absorbance on pH is shown in Fig. 1. The maximum appears in the region between pH 2·5 and 3·2.

Stability of Colour

The absorbance of a 4 p.p.m. solution of vanadium was measured after standing for 15 min and it was observed that the colour was stable for more than 1 h.

Interferences

Oxidising agents such as chromate and permanganate seriously interfere and must therefore be absent. Nickel, chromium and molybdenum, up to a concentration of 1000 p.p.m., can be tolerated while manganese and tungsten show no interference when present at a concentration 20 times that of vanadium. Iron(III), up to 200 p.p.m., can be masked with fluoride.

Complexing anions, such as fluoride, oxalate and tartrate, have no interfering effect, but free mineral acids must not be present; nitrite, peroxide, persulphate and other oxidising agents must also be absent. EDTA similarly interferes in the method if present in the solution.

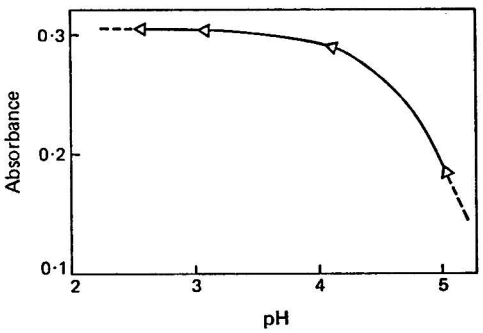

Fig. 1. Effect of pH on absorbance.

Method

Apparatus

Beckman H2 pH meter.
Unicam SP500 spectrophotometer.
Glass cells, 1 and 2 cm.

Reagents

o-*Phenylenediamine, 0·2 per cent. solution in ethanol.* Dissolve 0·2 g of *o*-phenylenediamine in 100 ml of 90 per cent. ethanol. Store the solution in an amber-glass bottle and prepare it freshly as required.

Sodium fluoride solution, 2 per cent. m/V. Dissolve 2 g of sodium fluoride in 100 ml of distilled water. Filter the solution and store it in a polyethylene bottle.

Standard vanadium(V) solution. Dissolve 2·2941 g of analytical-reagent grade ammonium vanadate in distilled water in a standard 1-l flask and make up to the mark with distilled water.

1 ml of solution ≡ 1 mg of vanadium.

Pipette 25 ml of this solution into a 250-ml calibrated flask and again make the volume up to the mark with distilled water.

1 ml of solution ≡ 0·1 mg of vanadium.

Preparation of Calibration Graph

Transfer, by use of a pipette, 0-, 1-, 2-, 3-, 4- and 5-ml portions of standard (0·1 mg ml^{-1}) vanadium solution into separate standard flasks of 50-ml capacity. To each add 5 ml of *o*-phenylenediamine solution and 10 ml of glacial acetic acid and shake well. Make the volume of each solution up to the mark with distilled water. The pH of the solution was measured by means of a pH meter and was found to be between 2·9 and 3·1. After 5–7 min determine the absorbance of each solution at a wavelength of 400 nm in a 1-cm cell and construct a graph relating these absorbances to the amount of vanadium, measured in milligrams. From the graph it is apparent that the reaction obeys Beer's law in the range 0·5–10 p.p.m. of vanadium.

Procedure

(*i*) *Procedure for high-speed steels*

High-speed steels generally contain 1–2 per cent. of vanadium. Dissolve 0·5 g of sample in 20–25 ml of dilute sulphuric acid (1 + 4) and oxidise it with a few drops of nitric acid. Add hydrofluoric acid dropwise until the tungsten present dissolves. Filter the solution on a paper-pulp pad and collect the filtrate in a 400-ml beaker, then wash the residue several times with hot distilled water. Ignite the residue in a platinum crucible and treat

it with hydrofluoric acid; if any residue is left fuse it with a small amount of potassium pyrosulphate. Next, cool the melt and dissolve it in 20 ml of sulphuric acid (1 + 9), warming to effect dissolution. Mix this solution with the filtrate in the 400-ml beaker and adjust the volume of the filtrate to between 100 and 150 ml with distilled water; cool the solution to below 15 °C. Add 0·1 N potassium permanganate solution dropwise until the pink colour persists, then add 0·5 ml in excess. After 5 min, remove the excess of permanganate by dropwise addition of 0·1 N sodium nitrite solution until the pink colour is just discharged.

Add 0·1–0·2 g of urea to the solution and heat to boiling. Cool it, and add ammonia solution (1 + 1) until a faint precipitate of iron begins to appear. Re-dissolve the precipitate in the minimum volume of dilute sulphuric acid (1 + 4). Then, transfer the solution quantitatively into a 500-ml calibrated flask and make the volume up to the mark with distilled water. Pipette 10 ml of the solution into a 50-ml standard flask and neutralise the solution with dilute ammonia solution (1 + 1), using phenolphthalein as indicator. Next, add 5 ml of sodium fluoride solution and 10–12 ml of glacial acetic acid and shake the mixture well until a clear solution is obtained. Add 5 ml of *o*-phenylenediamine and allow the colour to develop for 5 min. Make the volume up to the mark with distilled water, and determine the pH of the solution by using a pH meter. Measure the absorbance of the solution in a spectrophotometer with a 1- or 2-cm cell, whichever is suitable, and calculate the percentage of vanadium in the sample.

(*ii*) *Procedure for chromium - vanadium steels*

Chromium - vanadium steels generally contain 0·2–0·3 per cent. of vanadium. With such steels it is advisable to remove iron, either by extraction into diethyl ether or by electrolysis at a mercury cathode (as the iron content in the solution is very high, because of the large amount of sample required).

Dissolve 2·5 g of sample in dilute hydrochloric acid (1 + 1) and oxidise it with nitric acid, boiling off the nitrous fumes. Evaporate the filtrate down to a syrup and add to it 50 ml of hydrochloric acid (1 + 1). Filter the mixture through a paper-pulp pad, wash the residue several times with hydrochloric acid (1 + 9) and distilled water alternately until the residue is free from the matrix solution and ignite the residue. Then, treat the residue with hydrofluoric acid so as to remove silica and continue as described under *Procedure for high-speed steels* from "if any residue is left. . . ."

Evaporate the filtrate to about 50 ml and adjust the hydrochloric acid concentration to 5 M. Transfer the solution into a 100-ml separating funnel and wash the beaker with the minimum volume of 5 M hydrochloric acid. Cool the solution under running water, add a 20-ml portion of ether and shake the separator carefully, occasionally releasing the pressure inside the separating funnel. Allow the layers to separate and run the aqueous layer into a 250-ml beaker. Next, wash the sides of the separating funnel with 5 M hydrochloric acid and reject the ethereal layer, repeating the process until the whole of the iron has been removed. Drain the aqueous layer into the 250-ml beaker, washing the sides of the separating funnel with distilled water. Then, evaporate the aqueous solution on a water-bath in order to remove any dissolved ether. Cool the solution and to it add carefully 10 ml of sulphuric acid (sp. gr. 1·84); evaporate the solution on a hot-plate until free sulphur trioxide fumes are evolved. Cool it, and dilute to 100 ml with distilled water, warming to dissolve any solid matter.

Cool this solution to below 15 °C, add dropwise 0·1 N potassium permanganate solution and proceed as described under *Procedure for high-speed steels*, but transfer the solution into a 250-ml calibrated flask and make up to the mark with distilled water. Remove 10 ml of the solution with a pipette and determine the vanadium as described above.

Results

Some typical results for the determination of vanadium in BCS samples are shown in Table I.

Discussion

It is observed that even though iron(III) is masked by fluoride, after a period of 10–15 min a faint yellow colour begins to appear. Hence all measurements should be made within 10 min. If iron has been removed in the course of carrying out the method, no such precaution is necessary. The sensitivity of the reaction is found to be as low as 0·5 p.p.m. of vanadium.

TABLE I

DETERMINATION OF VANADIUM IN STEELS

Sample	Vanadium, per cent.	
	Certified value (average)	Found by this method
High-speed steel BCS 241/1	1·57	1·54 1·53
High-speed steel BCS 220/1	2·09	2·08 2·10
Chromium - vanadium steel BCS 224	0·24	0·22 0·22
Chromium - vanadium steel BCS 224/1 ..	0·19	0·17 0·18

We thank Dr. A. N. Choudhury, Chief Chemist, and Dr. N. R. Sen Gupta, Senior Chemist, Geological Survey of India, Calcutta, for their co-operation and help. Our thanks are also due to the General Superintendent, Durgapur Steel Plant, for permission to publish this paper.

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Received *May 3rd*, 1974
Accepted *August 14th*, 1974

The Determination of Trace Amounts of Vanadium in Titanium(IV) Chloride by X-ray Fluorescence Spectrometry

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A method is described for the determination of trace amounts of vanadium in titanium(IV) chloride involving pre-concentration and the use of X-ray fluorescence spectrometric techniques. The titanium(IV) chloride is added to a 40 per cent. solution of hydrofluoric acid and the mixture evaporated to a small volume. The vanadium is precipitated as the diethyldithiocarbamate complex at pH 5·0 in the presence of a co-precipitating agent, such as manganese(VII), and collected on a cellulose filter. The titanium is retained in solution by complexing it with malic acid. A lower limit of determination of 0·05 $\mu g\ g^{-1}$ of vanadium is obtained.

Titanium(IV) chloride is manufactured[1] by the chlorination of titaniferous materials at 700–1300 °C in the presence of a carbonaceous reducing agent. After being subjected to a series of condensation and scrubbing processes in order to remove major impurities, a crude product containing free chlorine and small amounts of dissolved compounds of iron, silicon and vanadium is obtained. Most of the impurities can be separated by distillation but vanadium cannot be separated by this method as it is present as vanadium oxychloride, which has a boiling-point similar to that of titanium(IV) chloride. It is necessary to add reducing agents, *e.g.*, silver, mercury, copper, iron, carbon, sulphides or organic compounds such as polymerised sulphonated oils, prior to distillation so as to convert the vanadium oxychloride into compounds of lower volatility. In the manufacture of titanium metal and titanium(IV) oxide pigments from titanium(IV) chloride, vanadium is a deleterious impurity and careful control must be maintained in order to keep its concentration below the critical limit of 5 $\mu g\ g^{-1}$.

The widest range of materials used for the determination of vanadium in titanium(IV) chloride are colorimetric reagents. Radcliffe and Parker[2] showed diphenylbenzidine to be satisfactory over the range 2–10 $\mu g\ g^{-1}$ of vanadium, but interference occurs from other oxidising agents such as iron(III) chloride, chlorine and chromium oxychloride. 4-(2-Pyridylazo)resorcinol has been investigated by Pal'nikova *et al.*,[3] and more recently by Pogranichnaya *et al.*,[4] and shown to be suitable over the range 1–20 $\mu g\ g^{-1}$ of vanadium. Zharovskiĭ and Pilipenko[5] have evaluated *N*-benzyl-*N*-phenylhydroxylamine and, after eliminating the interference due to titanium and iron by the addition of sodium fluoride and phosphoric acid, showed the method to have an optimum range of 0·01–0·3 per cent. of vanadium. Owens, Norton and Curtis[6] discovered that an intense yellow coloration was produced by the vanadium impurity when a sulphuric acid solution of titanium(IV) chloride was evaporated down with nitric acid.

Of the other techniques used for the determination of vanadium in titanium(IV) chloride, infrared spectroscopy[7–10] and gas - liquid chromatography[11] are too insensitive. Emission spectrography[12] has also been claimed to be a suitable technique for this determination. Jost and Bock[13] showed that atomic-absorption spectrometric analysis of the extracted tetraphenylarsonium chloro-complex of vanadium(III) enabled 0·72 $\mu g\ g^{-1}$ of vanadium in titanium(IV) chloride to be determined. Prudnevskiĭ *et al.*[14] showed that an optimum range of determination of 0·2–1 per cent. of vanadium was obtained when the vanadium - quinolin-8-ol complex was extracted into isoamyl alcohol and examined by atomic-absorption spectrometry. Coulometry was investigated by Piatnitskij and Jerisov[15] and shown to be capable of detecting 10 $\mu g\ g^{-1}$ of vanadium in a 5-g titanium(IV) chloride sample.

No reference was found to indicate that this determination was carried out by using X-ray fluorescence spectrometry, which is not surprising as it is impossible to determine trace amounts of vanadium in titanium compounds by direct X-ray fluorescence techniques due to overlap occurring between the principal vanadium line (Kα 0·2505 nm) and the titanium

Kβ line (0·2514 nm). The use of various analysing crystals, absorption filters and energy discriminative systems cannot overcome this problem. The other vanadium line (Kβ 0·2285 nm) is unsuitable because it has poor sensitivity and overlaps with the chromium Kα line (0·2290 nm). Therefore, this determination can be accomplished only by using an indirect method that involves chemical separation techniques, and a method based on work carried out by Luke[16] was devised.

Experimental

Reagents

All reagents should be of analytical-reagent grade when available.

Vanadium(V) solution. Prepare a solution containing 1000 μg ml^{-1} of vanadium by dissolving 2·294 g of ammonium metavanadate in water and diluting the solution to 1 l.

Titanium(IV) solution. Prepare a solution containing 1000 μg ml^{-1} of titanium by dissolving 1·667 g of titanium(IV) oxide, by heating with ammonium sulphate and concentrated sulphuric acid (sp. gr. 1·84), and diluting the solution to 1 l with water.

Manganese(VII) solution. Prepare a solution containing 1000 μg ml^{-1} of manganese by dissolving 2·870 g of potassium permanganate in water and diluting the solution to 1 l.

Iron(III) solution. Prepare a solution containing 1000 μg ml^{-1} of iron by dissolving 8·607 g of ammonium iron(III) sulphate in 100 ml of 10 per cent. sulphuric acid and diluting the solution to 1 l with water.

Cupferron solution, 1 per cent. m/V. Dissolve 1 g of cupferron in water, remove any insoluble matter by filtration and dilute the solution to 100 ml.

Buffer solution, pH 4. Dissolve 37 g of anhydrous sodium acetate in 500 ml of water, add 143 ml of glacial acetic acid and dilute the solution to 1 l with water.

Bromine solution. Add the required amount of bromine to water in order to give a saturated solution.

Boric acid solution, 5 per cent. m/V. Dissolve 5 g of boric acid in water and dilute the solution to 100 ml.

Malic acid solution, 10 per cent. m/V. Dissolve 10 g of malic acid in water and dilute the solution to 100 ml.

Sodium diethyldithiocarbamate.

Apparatus

The Pyrex filter holder (supplied by the Millipore Corporation of Bedford, Mass., USA) was as described by Luke,[16] with filter discs 25 mm in diameter and with a 0·8-μm pore size. The filter discs were removed from the filtration apparatus and mounted on titanium-free glass support discs with silicone grease, prior to measurement in the X-ray fluorescence spectrometer.

X-ray fluorescence measurements were made with a Philips PW 1540 total vacuum spectrometer using the following conditions: 1-kW tungsten-anode tube operating at 48 kV and 20 mA, lithium fluoride (200) analysing crystal with a 2*d* spacing of 0·4028 nm, flow-proportional detector using an argon - methane (9 + 1 *V*/*V*) gas mixture, 160-μm primary collimator, vacuum path, pulse-height selection and an analysis time of 100 s. A vanadium Kα line at 77·00° and a titanium Kα line at 86·21° were used.

Development of the Method

This work was an extension of the author's investigations[17] into the simultaneous determination of trace amounts of the first transition group metals in titanium(IV) oxide pigments by use of pre-concentration and X-ray fluorescence techniques. It had been shown that vanadium could be precipitated as the diethyldithiocarbamate complex in the presence of a suitable co-precipitating agent, while the titanium was retained in solution by complexing it with a hydroxycarboxylic acid such as citric, tartaric or malic acid.

In order to investigate the effect of pH and the complexing acid on the precipitation of vanadium, 10-ml portions of 10 per cent. *m*/*V* solutions of each of the acids were prepared containing 200 μg of vanadium and were adjusted to pH values within the range 3–9 by the addition of hydrochloric acid and ammonia solution. Sodium diethyldithiocarbamate (0·1 g)

was added to each solution so as to precipitate the vanadium, the suspensions were filtered by using the filter apparatus and, after mounting them on titanium-free glass support discs, the filters were dried at 105 °C. The intensity of the vanadium Kα line was measured under the conditions previously described. The results are shown in Table I, from which it can be seen that optimum precipitation occurs at a pH of 4·0 and in malic acid solution. However, there is little significant difference in the count rates at pH 4 and 5, and pH 5 is chosen as a slightly more stable manganese complex is formed at this pH value.

TABLE I

PRECIPITATION OF 200 μg OF VANADIUM AS THE DIETHYLDITHIOCARBAMATE COMPLEX OVER THE pH RANGE 3–9 IN 10 ml OF 10 PER CENT. *m/V* SOLUTIONS OF CITRIC, TARTARIC AND MALIC ACIDS

	Intensity/counts s^{-1}						
	pH 3·0	pH 4·0	pH 5·0	pH 6·0	pH 7·0	pH 8·0	pH 9·0
Citric acid	3628	3840	3690	3846	82	36	31
Tartaric acid	3307	3924	4302	3972	44	36	33
Malic acid	4306	5542	5526	4378	444	37	29

The effect of the co-precipitating agent was then investigated, and because of the non-specific complexing action of the diethyldithiocarbamate ion, a large selection of elements is available for assessment. Twenty micrograms of vanadium were precipitated from 10 ml of a 10 per cent. *m/V* malic acid solution at pH 5·0, and in the presence of 100 μg of various co precipitating agents. Cobalt, copper, nickel, iron, zinc, manganese, cadmium, lead and bismuth were investigated, and manganese was found to be the most suitable for this application because of the greater vanadium Kα line intensity obtained.

Hydroxycarboxylic acids are mild reducing agents and under certain conditions are capable of reducing the vanadium to the tervalent state. Vanadium(III) does not form an insoluble diethyldithiocarbamate complex and therefore the concentration of the malic acid must be kept to a minimum in order to obtain satisfactory precipitation efficiencies. This requirement was confirmed by examining the effect of increasing the volume of 10 per cent. *m/V* malic acid solution on the precipitation of 20 μg of vanadium and 100 μg of manganese(VII) with sodium diethyldithiocarbamate.

Calibration Graphs

Ten millilitres of a 10 per cent. *m/V* solution of malic acid were shown to be the minimum amount required to retain 1 ml of titanium(IV) chloride in solution at pH 5. Manganese(VII) was used as a co-precipitating agent in order to assist in retaining the vanadium in the quinquivalent state.

The required amount of vanadium(V) was added to a beaker containing 10 ml of the malic acid solution, 100 μg of manganese(VII) and 10 ml of water. The pH of the solution was adjusted to 5·0 with 50 per cent. *V/V* ammonia solution, and about 0·1 g of sodium diethyldithiocarbamate was added. The contents of the beaker were mixed, then allowed to stand for 2 min prior to filtration through a 0·8-μm Millipore filter. The filter was mounted on a titanium-free glass support disc with silicone grease, and the intensity of the vanadium Kα line was measured using the X-ray fluorescence spectrometer conditions outlined previously. In order to ensure that the amount of malic acid used under these conditions did not reduce the vanadium, the calibration procedure was repeated using 10 ml of the buffer solution. The comparative results are given in Table II. Both systems gave linear calibration graphs, and a sensitivity of 40 counts s^{-1} μg^{-1} was obtained for the malic acid solution. The theoretical limit of determination was calculated to be 0·05 μg of vanadium, and the precipitation efficiency in the malic acid solution was shown to be 90 per cent. This value was confirmed independently by atomic-absorption spectrometric analysis on 100 μg of vanadium. This recovery was acceptable considering the level of vanadium present in titanium(IV) chloride. The background level was determined by measuring the 0 μg vanadium standard filter at the wavelength of the vanadium Kα line.

Interferences

When this method was applied to hydrochloric acid solutions of titanium(IV) chloride to which known amounts of vanadium had been added, high count-rates were obtained on the vanadium Kα line. Examination showed this interference to be caused by titanium adsorbed on the precipitate. This interference was reduced to a reasonable level by increasing the volume of water used to wash the precipitate, but in order to obtain accurate results, a mathematical correction was necessary to compensate for the line overlap. This value was obtained by adding known amounts of titanium to 10 ml of buffer solution plus 100 μg of iron(III) to act as co-precipitant; 5 ml of cupferron solution were added, and, after mixing, the precipitate was collected on a 0·8-μm filter, mounted on a glass support disc, and the intensities of the titanium and vanadium Kα lines were measured. The results are given in Table III, and show that the interference due to titanium can be compensated for by multiplying the intensity of the titanium Kα line by 0·036, and subtracting this value from the intensity of the vanadium Kα line.

TABLE II

CALIBRATION RESULTS FOR THE DETERMINATION OF VANADIUM AS THE DIETHYLDITHIOCARBAMATE COMPLEX IN MALIC AND ACETIC ACID MEDIA

	Intensity/counts s^{-1}	
Vanadium/μg	Malic acid	Acetic acid buffer solution
0	35	35
5	223	239
10	437	478
15	670	685
30	840	925

Low and inconsistent results were obtained when the titanium(IV) chloride solutions containing the vanadium were subjected to this amended method, which were finally attributed to an increase in the concentration of vanadium(III) caused by the heat liberated when the pH was being adjusted to 5·0 with ammonia solution. Although neutralisation in the presence of ice gave higher recoveries, inconsistent values were still obtained. This supposition was confirmed when a 100 per cent. recovery was obtained when vanadium was added to cold titanium(IV) chloride solution that had previously been neutralised to pH 5·0.

TABLE III

EVALUATION OF THE CORRECTION FACTOR REQUIRED TO COMPENSATE FOR THE INTERFERENCE OF THE TITANIUM Kβ ON THE VANADIUM Kα LINE

	Intensity/counts s^{-1}					
Ti/μg	V Kα	Ti Kα	Background (B)	V Kα − B	Ti Kα − B	$\frac{\text{V K}\alpha}{\text{Ti K}\alpha}$
60	113	2500	18	95	2482	0·038
40	80	1732	18	62	1714	0·036
20	49	889	18	31	871	0·036

A method for removing the titanium prior to the application of the pre-concentration technique was then investigated. Solutions of titanium(IV) chloride in hydrochloric acid and containing known amounts of vanadium were made alkaline with sodium hydroxide. The hydrated titanium(IV) oxide was removed by filtration, leaving the vanadium in solution as sodium vanadate. The vanadium was determined by the co-precipitation method with the buffer solution and a good linear calibration graph was obtained. However, the sensitivity was found to be 32 counts s^{-1} μg^{-1}, which corresponds to only a 70 per cent. recovery of vanadium. Attempts to modify this technique so as to obtain higher percentage recoveries were unsuccessful and so this approach was abandoned.

The method of retaining the titanium in solution by complexing it with malic acid was re-investigated. The failure of this technique had been shown to be caused by reduction of the vanadium(V) to vanadium(III) by the heat produced at the neutralisation stage, and a means of reducing the acidity was sought. This was accomplished by adding the titanium(IV)

chloride to a 40 per cent. solution of hydrofluoric acid, and evaporating to a small volume in a PTFE beaker. Initially, recoveries of 23–26 per cent. were obtained; however, addition of boric acid to the solutions prior to the addition of malic acid and co-precipitation of the vanadium increased the recovery to 42–49 per cent. Recoveries in excess of 90 per cent. were obtained by addition of boric acid to the evaporated hydrofluoric acid solutions, followed by an excess of a saturated solution of bromine. The excess of bromine was removed by warming, and the solution was re-cooled prior to the addition of the malic acid solution and subsequent precipitation stage. The low concentration of impurities in this grade of titanium(IV) chloride that precipitate as the diethyldithiocarbamate complex under these conditions gives a cellulose filter that is stable and does not crack or powder on drying. Application of this technique to crude titanium(IV) chloride could result in thick unstable cellulose filters being obtained; this effect can be overcome by using a smaller volume of sample.

Recommended Procedure for the Determination of Vanadium in Titanium(IV) Chloride

Transfer 1·00 ml of titanium(IV) chloride from a clean dry pipette into a PTFE beaker containing 5 ml of a 40 per cent. solution of hydrofluoric acid. The titanium(IV) chloride should be allowed to trickle down the wall of the tilted beaker into the hydrofluoric acid solution. Evaporate the solution down to a volume of about 1 ml on a hot-plate thermostatically controlled at 220 °C. Cool and add 5 ml of the boric acid solution and boil for 5 min. Add, dropwise, an excess of bromine solution, allow the mixture to stand for 5 min and then heat it on the hot-plate until the excess of bromine is removed. Thoroughly cool and add 10 ml of the malic acid solution. Neutralise to pH 5·0 with ammonia solution keeping the temperature of the solution below 20 °C, then filter it through a 0·8-μm filter in order to remove any colloidal titanium(IV) oxide that may have formed. Transfer the solution into a 100-ml beaker and add 100 μg of manganese(VII). Add about 0·1 g of sodium diethyldithiocarbamate, mix and allow to stand for about 2 min. Filter the solution through a 0·8-μm filter, wash the filter well with water and mount it on a titanium-free glass support disc using silicone grease. Dry the disc at 105 °C for 10 min and measure the intensities of the vanadium and titanium Kα lines.

Results

Recoveries of 91–102 per cent. were obtained when the recommended procedure was applied to "pure" titanium(IV) chloride samples to which known amounts of vanadium in the range 2·5–100 μg were added, the vanadium Kα line being measured and compared against standards prepared from pure aqueous solutions of vanadium.

Five samples were analysed by this technique and the results are compared with those of the diphenylbenzidine colorimetric method in Table IV. Samples 2–4 inclusive were analysed eight times and the mean values together with the 2σ relative standard deviations are tabulated in Table V.

TABLE IV

DETERMINATION OF VANADIUM IN TITANIUM(IV) CHLORIDE SAMPLES BY THE CO-PRECIPITATION X-RAY FLUORESCENCE SPECTROMETRIC METHOD

	Intensity/counts s^{-1}							V/μg g^{-1} by—	
	V Kα	Ti Kα	V Kα − B	Ti Kα − B	(Ti Kα − B) × 0·036	V Kα corrected for Ti Kβ	V/μg	colorimetry	X-ray fluorescence
Vanadium, 20 μg	828	—	805	—	Sensitivity ≡ 40·25 counts s^{-1} μg^{-1}				
Vanadium, 0 μg	23	—	—	—					
Sample 1	37	292	14	269	10	4	0·10	<0·5	0·06
2	123	1984	100	1961	71	29	0·72	0·6	0·42
3	69	172	46	149	5	41	1·0	0·8	0·58
4	281	703	258	680	24	234	5·8	3·2	3·4
5	1645	236	1622	213	8	1614	40·0	22	23·1

TABLE V

STATISTICAL ANALYSIS OF THE RESULTS OF EIGHT DETERMINATIONS ON THE SAME SAMPLE OF TITANIUM(IV) CHLORIDE

Sample	Mean value/μg g^{-1}	2σ relative standard deviation, per cent.
2	0·43	15·2
3	0·55	18·6
4	3·3	8·8

The results show that the method is suitable for the determination of trace amounts of vanadium in titanium(IV) chloride, and a result can be obtained in about 45 min. In practice, this method was found to give a 2σ relative standard deviation of about 15 per cent. with a lower limit of determination of 0·05 μg g^{-1} of vanadium.

The Directors of Tioxide International Limited are thanked for permission to publish this paper. The author also acknowledges the technical assistance of Mr. M. C. Dobson.

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Received *August 19th*, 1974
Accepted *November 7th*, 1974

Device for Trace Analysis for Fluorine in Reaction Tubes by Atomic-absorption Spectroscopy

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An analytical method is described for the detection of trace amounts of fluorine by atomic-absorption spectroscopy. Sodium vapour is made to react with fluorine-containing compounds at temperatures of about 800 °C, and, under certain conditions, the decrease in the atomic sodium concentration gives a relative and specific value for the amount of fluorine present. The best instrument parameters for the experimental determination were measured and theoretically interpreted; 0·8 ng of fluorine was found to be the detection limit. As an example of the practical importance of this technique of trace analysis for fluorine, its application as a fluorine-specific detector in the gas chromatography of trifluoroethanol is described.

It is well known that sodium reacts with fluorine in absorption tubes at relatively low temperatures (about 700 °C).[1–3] Use has been made of this principle to evolve an indirect method for determining trace amounts of fluorine by means of atomic-absorption spectroscopy. The following investigation was undertaken in order to ascertain the best instrument parameters for obtaining detection limits as low as possible.

Experimental

Measuring Equipment

A diagram of the device used is shown in Fig. 1. A sodium vapour spectral lamp (Osram) serves as background source, the emission being converted into modulated light of 300 Hz with a Brookdeal chopper, Type 9479. This modulated light is aligned with a parallel beam of light by means of a lens. The beam passes through one of the absorption tubes described below. The diameter of the beam is adjusted so that it is about two thirds that of the tube and it is arranged that the beam, when passing through the tube, does not make contact with the inner face of the tube, thus excluding random phenomena. With a second lens the beam from the lamp is projected on to the entrance slit of the monochromator (Bausch & Lomb, 0·5-m grating, Type 534 UB, blaze angle for 300 nm). The slit widths are 0·1 mm, corresponding to a spectral band width of 0·25 nm. The monochromator is

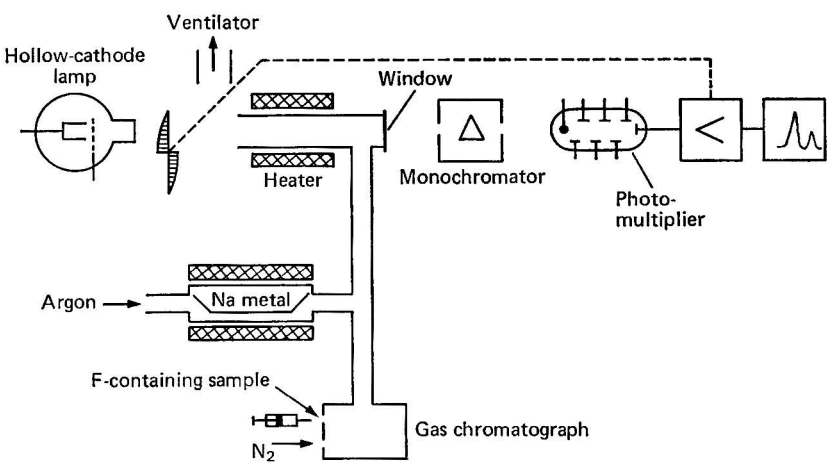

Fig. 1. Device for the determination of fluorine.

adjusted on the spectral doublet of sodium (589 nm). This light, separated by spectral means, is directed on to an RCA 1 P28 photomultiplier, which is operated with potentials ranging between 750 and 850 V. The photo-currents are led to a lock-in amplifier (Electronics, Missiles and Communications Inc., Mount Vernon, New York, Type EMC 394). The reference voltage for the lock-in amplifier is taken directly from the chopper. The recorder operates with chart (Kipp & Zonen, Type BD9) speeds of up to 20 mm min^{-1}.

Procedure

All the reaction tubes (see Table I) are charged with sodium vapour in order to obtain a quasi-stationary equilibrium. This equilibrium is achieved as follows. In an electrically heated furnace (Heraeus, Hanau, Type B/A 1.7/10) a flow of argon is passed through a quartz tube of 10 mm i.d. and 160 mm length, the optimum volume passed depending on the size of the reaction tube. A porcelain cell (Staatliche Porzellan Manufaktur, Berlin, Type h 00) charged with about 0·3 g of metallic sodium is placed in the quartz tube. The temperature of the furnace should be about 300 °C for optimum conditions in the reaction tubes.

TABLE I

DIMENSIONS OF REACTION TUBES

Designation of tube	Internal diameter/mm	External diameter/mm	Heated length of tube/mm
a	3·2	5·4	100
b	4·1	12·1	100
c	5·7	8·3	100
d	8·1	10·7	100
e	8·1	10·7	50
f	8·1	10·7	200
g	10·1	12·7	100
h	12·4	15·0	100

About 0·1 μl of mixtures of trifluoroethanol and dibutyl ketone in proportions between 1 + 1 and 1 + 2000 is introduced by means of a gas chromatograph (Perkin-Elmer, Type F20H) operated under the following conditions: column material, stainless steel; temperature of column, 160 °C; packing material, polyethylene glycol OS 12·14 on a siliceous earth support; and carrier gas, nitrogen at the flow-rate of 44 ml min^{-1}. The effluent from the gas chromatograph is diluted with the above-mentioned sodium vapour - argon stream by use of a T-piece, and the mixture is then led to one end of the reaction tube by a lateral quartz connecting piece. This end of the tube, which faces the monochromator, is closed with a glass window and, so that it can be cleaned occasionally, the window is secured to the ground end of the reaction tube simply with a spring. The other end of the reaction tube is open. The waste gas is removed via an exhaust, with a view to obtaining a well defined length of absorption.

Results and Discussion

Best Range of Extinction

First, it is necessary to determine the range of extinctions corresponding to the lowest levels of fluorine. The law of absorption takes the form

$$I = I_0 e^{-K_n l} \qquad (1)$$

With a constant length, l, of the reaction tube, the variation of the intensity, I, due to a small variation of the extinction, K_n, is given by

$$\frac{\partial I}{\partial K_n} = -l I_0 e^{-K_n l} \qquad (2)$$

It is evident that the most favourable range of extinction occurs in the case when $\frac{\partial I}{\partial K_n}$ [equation (2)] is a maximum, depending on the value of l. Therefore, the optimum theoretical length of the reaction tube can be calculated from

$$\frac{\partial^2 I}{\partial K_n \partial l} = 0$$

This equation gives the solution

$$K_n l = 1 \qquad (3)$$

The theoretical tube length derived above does not take into consideration the greater effective tube length that is influenced by the mechanism of the reaction (see below). Experimentally, the coefficient of extinction, K_n, depends directly on the flow-rate of argon as well as on the temperature of the furnace (300 °C for an extinction of 0·4). These relationships can be used in order to obtain the optimum conditions for determining the detection limit of fluorine.

That the decadic extinction of about 0·4 is in fact the optimum has been verified by other tests. Therefore, we have fixed the starting extinction of sodium vapour at about 0·4, by variation of the temperature in the sodium vaporisation furnace. It must be mentioned here that this optimum value for the vaporisation of sodium varies to some extent with different flow-rates of argon. This effect is caused by the influence of the argon on the dilution of the sodium vapour and therefore on the extinction of sodium vapour (K_n) in the reaction tube.

Optimum Reaction Temperature

For the reaction tubes a–h (Table I) we varied the temperature of the furnace for each tube and determined the corresponding extinctions. That temperature which yields the highest sensitivity is designated the optimum reaction temperature (see below). If the tubes with unusual lengths (e and f) and the tube with an especially thick wall (b) are not at first taken into consideration, it is observed that for the remaining tubes the optimum temperature lies between 800 and 900 °C and, accordingly, that the higher temperatures are valid for the tubes with the greater internal diameters.

These results can be interpreted as follows. There exists within each tube a temperature gradient from the external to the internal surface, because the heat is applied to the external surface of the tube while a stream of cool gas flows through it, the gas furthest from the surface having the highest velocity, corresponding to the profile of gas flow in tubes. Therefore, it is necessary, in order to produce similar temperature gradients, to intensify the heating of those tubes with greater diameters. Corresponding conditions will apply to tubes with greater wall thickness. The problem of heating tubes of different lengths is dealt with below.

Effect of Temperature

Interest was centred on the change in the measurable signal produced by addition of fluorine (*i.e.*, the change in the extinction of the sodium vapour when influenced by fluorine) if the temperature in a reaction tube was varied systematically. This temperature dependence is of interest because if the 50 per cent. band width (full width at half maximum; F.W.H.M.) of this temperature (the curve is nearly Gaussian, as shown by the example in Fig. 2) is very small, it is necessary to maintain good temperature stability in the reaction tube; the tube must therefore be heated at a constant temperature.

When the temperature dependences of the signals are measured for the above different reaction tubes, it is found that the 50 per cent. band width, ΔT, a quantity representing the temperature dependence, depends in a characteristic manner upon the internal diameter of the tube. The 50 per cent. band widths are practically identical ($\Delta T = 155$ °C) for the tubes with the smallest and the greatest internal diameters (tubes a and h, respectively); on the other hand, for tubes with an intermediate internal diameter (tubes c and d) the 50 per cent. band width occurs at 65–85 °C. It is of interest to note that the optimum limit of sensitivity is also situated in this temperature range (see below).

It is evident that with highly increased temperatures, the conditions will become unfavourable, due to the onset of a noticeable degree of dissociation. This is also true for low temperatures, because the formation of the required sodium fluoride will decrease. These considerations may explain the optimum extinction for sodium vapour at intermediate temperatures.

Flow-rate of Argon Through the Sodium Vaporisation Furnace

When the flow-rate of argon is varied and the other conditions are maintained constant, the measurable fluorine signal will generally change. First, an optimum flow-rate of argon is required (*i.e.*, that which gives the highest possible measurable fluorine signal above the level

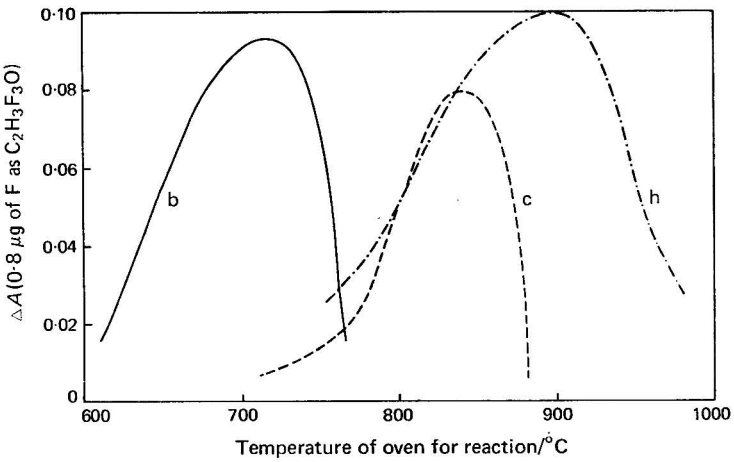

Fig. 2. Temperature dependence of signal for different reaction tubes. Internal diameter of tube: b, 4·1 mm: c, 5·7 mm; and h, 12·4 mm (see Table I).

of disturbance effects observed in tubes with different diameters). An optimum flow-rate of argon of 500 ml min^{-1} is needed for tube diameters between 6 and 8 mm; with small tube diameters, the flow-rate of argon required is appreciably reduced (180 ml min^{-1}), while with the largest tube diameter a flow-rate of 320 ml min^{-1} is required.

If, instead of determining the optimum fluorine signal as a function of the tube diameter, we examine the dependence of all measurable signals on the argon flow-rate, with the diameter of tubes constant, we again find that the optimum measurable signals occur at argon flow-rates of 500–700 ml min^{-1} with medium tube diameters; for all other tube diameters, smaller measurable signals are obtained and their maxima are displaced to lower argon flow-rates. This is true for both very small and very large tube diameters.

In other words, if we can imagine that the tube diameters decrease while the flow-rate of argon is kept constant, then the gas flow-rate will increase such that one gas-chromatographic peak flowing through the reaction tube (with decreasing diameter) becomes longer than the optical path length of the reaction tube. An increasing proportion of the peak will therefore have no effect on the optical signal and the latter will accordingly be lowered.

If the optimum flow-rate determined by the measurements is exceeded, it becomes necessary to reduce the amount of sodium in order to avoid excessive dilution of the fluorine. Because the duration of the gas-chromatographic peaks is about 1 s, only a small portion of the tube contains sodium fluoride, the remainder containing sodium vapour. Accordingly, the measurable extinction becomes smaller than under optimum conditions. Theoretical calculations of the experimentally determined parameters prove that when the absorbance is at a maximum a gas-chromatographic fraction comprises the entire length of the tube.

Detection Limits

The detection limit has been defined by Kaiser[4] and later by IUPAC as follows:

$$x = \bar{x}_{bl} + 3\, s_{bl}$$

where

x = reading at the detection limit;

s_{bl} = calculated scatter of the blank reading, given by the standard deviation (s_{bl}) of the 20 blank readings (= "analytical noise");

$\bar{x}_{bl}$ = calculated average of the blank readings.

From the analytical function, $c = f(x)$, the fluorine concentration, c, at the limit of detection

follows. Table II shows the detection limits found with the different tubes under optimised conditions of measurement.

TABLE II

FLUORINE DETECTION LIMITS FOR DIFFERENT REACTION TUBES

Designation of tube	Internal diameter/mm	Heated length of tube/mm	Detection limit of F/ng
a	3·2	100	12·0
b	4·1	100	7·0
c	5·7	100	2·4
d	8·1	100	1·9
e	8·1	50	1460·0
f	8·1	200	0·8
g	10·1	100	3·0
h	12·4	100	7·2

It can be seen that the best detection limit is obtained with the tube of 8·1 mm internal diameter and for the longest heated length of tube. Changing from the most satisfactory tube of 8·1 mm i.d. and 200-mm heated length to a similar tube with 100-mm heated length, the detection limit is raised slightly (detection limit 1·9 instead of 0·8 ng). The extremely poor detection limit (1460 ng) obtained with the tube of similar internal diameter but with only 50-mm heated length is surprising, but this discrepancy, which is contrary to simple theory, can be explained by the fact that a portion of the tube is needed for the diffusion and dilution of the vapour and for the reaction. The portion of the tube that cannot be used for the absorption measurement will be greater with shorter tubes than with longer tubes. If we compare all the tubes of equal length (100 mm) but different diameters, the optimum is well defined with the internal diameter of 8·1 mm. Previous optimising investigations have already shown that this diameter should give the best detection limits, the reasons for which are given above.

Reproducibility

A 1 + 50 mixture of trifluoroethanol and dibutyl ketone was used, 0·1 μl containing 1·6 μg of fluorine being introduced into the gas chromatograph. The fluorine signal was measured 20 times. It was assumed, of course, that this concentration occurs on the linear portion of the calibration graph. The mean relative standard deviation of the measurable signals is about $\pm$6·4 per cent. A better result would be obtained if the measured signals were plotted in relation to measured signals of standard dilutions at similar concentrations.

Calibration Graph

The calibration graph for the tube d is linear between the detection limit and 1·6 μg of fluorine, and then forms a plateau. The linear portion of the calibration graph for tube f occurs up to 0·16 μg of fluorine. For the required degree of accuracy, one or two decimal places in the values read from the linear calibration graph can be omitted. If non-linear calibration characteristics are included in special cases, it will be necessary to omit more decimal places. At this juncture linearisation of calibration graphs by electronic means should be considered.

Specificity of the Method

Normally, spectroscopic gas-chromatographic detectors have better specificities than the usual detectors. In the proposed indirect atomic-absorption spectroscopic method attention has been paid to the fact that sodium also reacts with other halogens. We therefore determined the absorbances of sodium fluoride, chloride, bromide and iodide at equal concentrations. At a temperature of 800 °C in the reaction tube no absorption of chlorine could be detected. The absorbances of equal amounts of the other two halogens relative to fluorine, taken as unity, were bromine 0·05 and iodine 0·19.

Investigation of the Reaction Mechanism

The experiments described above do not clearly establish in which part of the apparatus the formation of sodium fluoride has completely taken place. A T-piece was included in the above apparatus, in which the gases were pre-mixed. In order to determine whether the T-piece is necessary or not, a reaction tube of 8·1 mm i.d. and 100-mm length, with two connecting branches, one for sodium plus argon and the other for the diluted fluorine compound, was used. These experiments established that:

(*i*) the desired formation of sodium fluoride takes place without pre-mixing;

(*ii*) the measurable extinctions in geometrically equal tubes with one constituent per branch are 1·5 and 2 times lower than those for the tubes with previous mixing by use of the T-piece.

Without pre-mixing of the reagents, a portion of the reaction tube is used for the desired mixing, heating and final reaction before the procedure is completed, indicating that part of the reaction zone is not available. The experiment also shows that in travelling from the T-piece to the reaction tube only a very small amount of the sodium fluoride escapes, compared with that which escapes from the tube with two branches. From this experiment it can be concluded that previous mixing of the reaction components provides favourable conditions, because the length of the reaction tube is more efficiently utilised. It is further concluded that the efficiency of the determination of fluorine with the stoicheiometric mixture of both elements or with supersaturation with sodium vapour must be 100 per cent., because no fluorine remains.

The authors gratefully acknowledge the financial assistance given by the Deutsche Forschungsgemeinschaft, Bonn.

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Received *June 11th*, 1974
Accepted *September 17th*, 1974

Determination of Trace Levels of Barium in Calcium Carbonate by Atomic-absorption Spectrophotometry

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A sensitive atomic-absorption spectrophotometric method for the determination of trace levels of barium in calcium carbonate using a simple graphite-rod atomiser has been developed. The calcium carbonate is dissolved in nitric acid and the solution applied to the sample cavity in the graphite rod. A detection limit of 0·0045 μg ml^{-1} of barium in a solution containing 10 000 μg ml^{-1} of calcium was obtained on a 5-μl sample volume.

The determination of low levels of barium in the presence of large amounts of calcium using flame-spectroscopic techniques is difficult.[1–3] The atomic-absorption limit of detection for barium, even in the absence of calcium, is generally stated to be in the range 0·02–0·1 μg ml^{-1}. The presence of large amounts of calcium tends to degrade this limit owing to an increased noise level caused by intense emission from the CaOH band at the barium resonance line wavelength of 553·6 nm. Bano[2] and Kawamura *et al.*[3] have recommended the chemical separation of barium from calcium prior to determination of the barium by atomic-absorption spectrophotometry. Rubeška[4] has used a nitrogen-shielded nitrous oxide - acetylene flame in order to reduce the CaOH emission by increasing the volume of the interconal zone, thereby minimising the concentration of OH radicals.

The flame-emission technique in which the nitrous oxide - acetylene flame is used is more sensitive for pure barium solutions than the absorption method. However, the presence of a large excess of calcium causes the small barium emission signal to be swamped by the intense CaOH background emission. Various instrumental refinements have been suggested in order to overcome this limitation, for example, the use of a nitrogen-shielded flame,[4] the use of a high-resolution echelle spectrophotometer,[5] automatic background correction using an adjacent wavelength[6,7] and automatic subtraction of the background emission using a synthetic blank solution.[8] With automatic background correction a detection limit of 0·1 μg ml^{-1} of barium in a 2000 μg ml^{-1} calcium solution was obtained.[6]

The flameless atomisation technique appears to be the ideal method for the determination of barium in calcium carbonate, the barium being atomised at a high temperature with negligible background emission from the calcium sample matrix. Renshaw *et al.*[9,10] found that the sensitivity for barium obtained with a graphite-tube atomiser was relatively poor, but if the tube was lined with tantalum foil a 20-fold improvement in sensitivity was observed. A detection limit of 1×10^{-10} g of barium was obtained when using the tantalum foil. The low sensitivity with the plain graphite tube was attributed to carbide formation.

In this paper a sensitive atomic-absorption spectrophotometric method for the determination of trace levels of barium in calcium carbonate, in which a simple graphite-rod atomiser is used, is reported. The calcium carbonate is dissolved in nitric acid and the solution applied to the sample cavity in the graphite rod.

Apparatus

A Shandon Southern A3470 flameless atomiser and an A3400 atomic-absorption spectrophotometer were used. The output from the A3400 was monitored on a Shandon Southern Autograph Recorder (0·5-s full-scale deflection). The temperature of one of the air-cooled graphite-rod head pillars was monitored by use of a thermistor and the A3470X19 temperature indicating unit. The apparatus has previously been described.[11]

An Oxford 5-μl pipette with disposable PTFE tips (Boehringer Corp. Ltd.) was used to apply the sample to the rod.

Gases

High-purity argon and methane - argon (1 + 9 *V*/*V*) were used, the two gases being mixed prior to entry into the graphite-rod head. The presence of a small amount of methane in

the inert gas surrounding the graphite rod resulted in the formation of a pyrolytic graphite coating and considerably reduced the non-specific background absorption that arose from the calcium matrix.

Reagents

Calcium solution, 50 000 $\mu g\ ml^{-1}$. Spectroscopically pure calcium carbonate (24·97 g; Johnson Matthey Chemicals Ltd.) was dissolved in 150 ml of 4 M nitric acid (Aristar grade) and the solution diluted to 200 ml with distilled water.

Barium stock solution, 1000 $\mu g\ ml^{-1}$. Barium chloride standard solution for atomic-absorption spectrophotometry, BDH Chemicals Ltd.

Glassware was soaked in 25 per cent. V/V nitric acid prior to use. All solutions were prepared just before use.

Optimisation of Operating Parameters

Rod type

A Type 2 graphite rod was used.[11] The alternative Type 1 rod has a much shorter lifetime (about 40 firings) than the Type 2 rod (about 80 firings) for this application.

Sheath Gas Supply

A four-fold reduction in signal, which was attributed to nitride formation, was observed with pure barium solutions if nitrogen was used in place of argon. The optimum gas flow-rates were 2·5 l min^{-1} for argon and 0·20 l min^{-1} for methane - argon (1 + 9 V/V).

Atomisation Voltage and Time

The aperture height was initially set by passing a No. 51 drill blank (1·7 mm diameter) through the two 1·8 mm diameter apertures, and lowering the aperture height until slight pressure could be felt between the top of the rod sample cavity and the drill blank.

An atomisation time of 1·5 s was used. The atomisation voltage was then set to give a small signal (0·03–0·04 absolute absorbance unit), which arose from volatilised graphite. This procedure was carried out by using a lead hollow-cathode lamp with the wavelength set to 283·3 nm. If the atomisation voltage was set up using the 553·6 nm barium line, the black-body emission from the rod was so intense that overload of the demodulator occurred. The setting-up procedure for the atomisation voltage was highly critical. If the voltage was set too low memory effects and poor resolution between the barium and graphite peaks were observed, and if set too high the lifetime of the rod was short.

When a new graphite rod was inserted into the graphite-rod head it was initially fired three times, with the argon supply turned off and the methane - argon supply set to give a flow of 1·5 l min^{-1}. This procedure resulted in the formation of a pyrolytic graphite coating over the heated region of the graphite rod.

Aperture Height Setting

After the atomisation voltage had been set up as described above the lead lamp was replaced by a barium lamp and the wavelength set to 553·6 nm. The rod was then fired and the "dry" blank trace recorded. The aperture was then raised in 0·1-mm steps and the procedure repeated until the recorded trace did not show a decrease in absorbance (due to demodulator overload from the intense thermal emission at 553·6 nm) prior to the final graphite absorption peak (Fig. 1). The barium signal was almost completely resolved from the graphite absorption peak (Fig. 1). The optimum aperture height was found to be 0·25–0·4 mm above grazing incidence. It was essential to set the atomisation voltage with the aperture set to grazing incidence using an intense line in the ultraviolet region, thus ensuring that the onset of graphite volatilisation could be accurately monitored. If the final aperture height setting was too low demodulator overload occurred, and if set too high background (non-specific) absorption from the calcium matrix increased.

Barium Hollow-cathode Lamp

A neon-filled Southern Spectral Sources barium hollow-cathode lamp, run at 14 mA, was used. If the lamp current was appreciably reduced or an old wide-bore (much less intense)

barium lamp was used, overload of the demodulator from the intense thermal emission from the graphite rod was observed.

The minimum band pass of 0·18 nm was used.

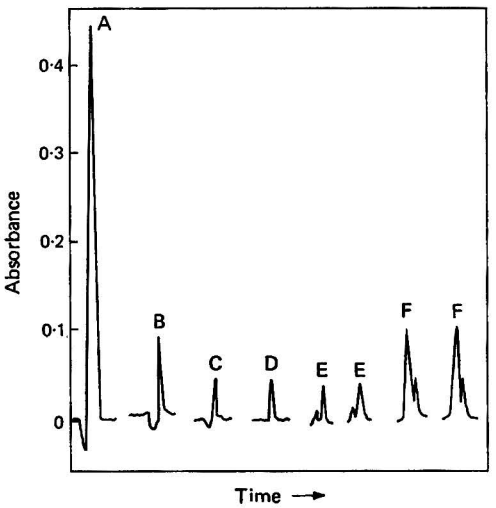

Fig. 1. Adjustment of aperture height. Flow-rates: argon 2·5 l min^{-1}; methane - argon (1 + 9 *V*/*V*) 0·2 l min^{-1}. Barium lamp, λ = 553·6 nm. A, Dry blank, aperture set to grazing incidence; B, as A, aperture raised 0·1 mm; C, as A, aperture raised 0·2 mm; D, as A, aperture raised 0·3 mm; E, 5 μl of 10 000 μg ml^{-1} calcium solution (aperture as D); and F, 5 μl of 10 000 μg ml^{-1} calcium + 0·1 μg ml^{-1} barium solution (aperture as D).

Background (Non-specific) Absorption Measurements

In order to determine the background (non-specific) absorption due to the calcium matrix, the ytterbium 557·6 nm non-resonance line was used. The ytterbium lamp current was adjusted so as to give a similar intensity to the barium line. Many other element lamps were tested but no suitably intense line between 550 and 556 nm was found. A number of low-intensity lines (compared with the barium 553·6-nm line) were found, but with these overload of the demodulator (see previous section) occurred.

The 541·0-nm chromium line was sufficiently intense when the chromium lamp was run at 17 mA, gave background signals similar to those of the 557·6-nm ytterbium line and could be used to monitor background absorption. By using the optimum operating conditions the background absorption signal for 5 μl of 10 000 μg ml^{-1} calcium solution corresponded to 0·008 μg ml^{-1} of barium.

Optimum Methane Flow-rate

The addition of methane to the argon purge gas was found to result in the formation of a pyrolytic coating that substantially increased the lifetime of the rod,[11] especially in the presence of large amounts of calcium. The effect of increasing the flow-rates of the methane - argon on the barium response obtained from a solution containing 0·1 μg ml^{-1} of barium and 10 000 μg ml^{-1} of calcium is shown in Fig. 2. This figure also shows the decrease in the background (non-specific) absorption, as measured when using the ytterbium 557·6-nm line, with increasing methane flow-rate. When propane was used instead of methane only a small decrease in the background absorption was observed.

A flow-rate of 0·20 l min^{-1} of methane - argon (1 + 9 *V*/*V*) was used with an auxiliary argon flow-rate of 2·5 l min^{-1}.

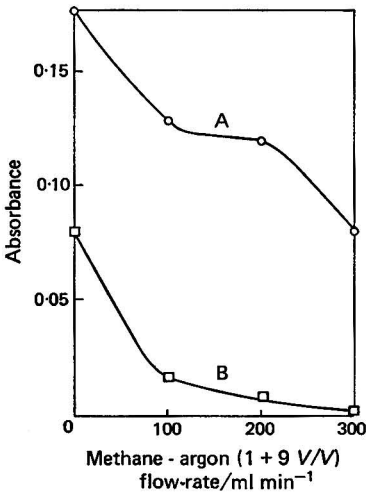

Fig. 2. Effect of methane - argon (1 + 9 *V*/*V*) flow-rate. Argon flow-rate 2·5 l min^{-1}. A, 5 μl of 10 000 μg ml^{-1} calcium + 0·1 μg ml^{-1} barium solution (barium lamp, λ = 553·6 nm); and B, 5 μl of 10 000 μg ml^{-1} calcium solution (ytterbium lamp, λ = 557·6 nm).

Effect of Calcium on the Barium Response

Fig. 3 shows the effect of increasing levels of calcium upon the barium response. Although it was possible to obtain results with solutions containing 20 000 μg ml^{-1} of calcium, this level of calcium caused problems with mechanical loss during the dry-ashing stage and also shortened the lifetime of the rod. These drawbacks were attributed to a reaction occurring between the calcium and the graphite. A calcium concentration of 10 000 μg ml^{-1} was considered to be the optimum and gave a rod lifetime of approximately 80 firings. The increase in response on adding calcium was attributed to preferential carbide formation by the calcium.

Setting the Dry-ashing Voltages

The second dry-ashing voltage was set to give a rod temperature of bright red heat in order to decompose the calcium nitrate, the first dry-ashing voltage being set to two thirds of the second dry-ashing voltage. The timers for these two channels were set to 12 s. After the second dry-ash channel had been operating for 9 s, the rod power was switched off, the rod allowed to cool for 5 s and then fired to atomise the sample. If the rod was fired directly after the second dry-ashing stage without an intermediate cooling period it was very difficult to set the atomisation voltage so as to give a reproducible graphite peak.

Method

The dried calcium carbonate sample (2·497 g) was dissolved in 15 ml of 4 M high-purity nitric acid and the solution diluted to 100 ml with distilled water. This solution contained 10 000 μg ml^{-1} of calcium. Suitable barium standards containing up to 0·5 μg ml^{-1} of barium and 10 000 μg ml^{-1} of spectroscopically pure calcium were prepared.

A new graphite rod was inserted and coated with pyrolytic graphite (see above). Five microlitres of 10 000 μg ml^{-1} calcium blank solution were applied to the rod and the rod was fired; this procedure was repeated six times and was necessary in order to "run in" the rod. A dry blank (with no sample) was then run. When the rod pillar temperature had cooled to 50 °C, 5 μl of a suitable standard or the sample were applied to the rod sample cavity and the output trace recorded. Another dry blank was run before the next sample was added. If a sample gave a signal that corresponded to more than 0·5 μg ml^{-1} of barium

the solution was diluted with the 10 000 μg ml^{-1} spectroscopically pure calcium standard. The procedure of running a sample or standard followed by a dry blank overcame a slight memory effect that was sometimes observed, especially with barium concentrations above 0·3 μg ml^{-1}

Results

The calibration graph is shown in Fig. 4. The characteristic concentration and 2σ detection limits for 5 μl of a solution containing 10 000 μg ml^{-1} of calcium were 0·0035 μg ml^{-1} (1·75 $\times$ 10^{-11} g) and 0·0045 μg ml^{-1} (2·25 $\times$ 10^{-11} g), respectively. The background (non-specific) absorption signal from 5 μl of this solution was equivalent to 0·008 μg ml^{-1} of barium. The relative standard deviation at the 0·1 μg ml^{-1} of barium level (11 results) was 4·3 per cent. The barium level in the 10 000 μg ml^{-1} calcium blank solutions prepared from two different batches of spectroscopically pure calcium carbonate corresponded to 0·010 μg ml^{-1} and 0·021 μg ml^{-1}.

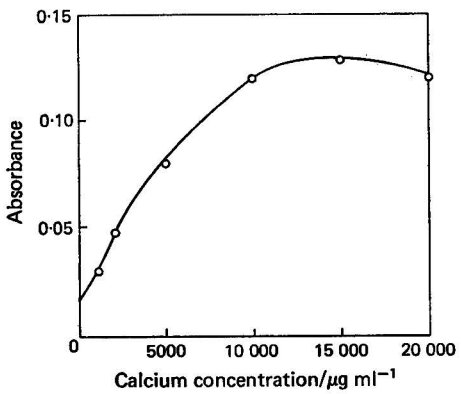

Fig. 3. Effect of increasing calcium concentration. Flow-rates: argon 2·5 l min^{-1}; methane - argon (1 + 9 *V*/*V*) 0·2 l min^{-1}. 5-μl sample volumes. Solutions contained 0·1 μg ml^{-1} of barium. Barium lamp, λ = 553·6 nm.

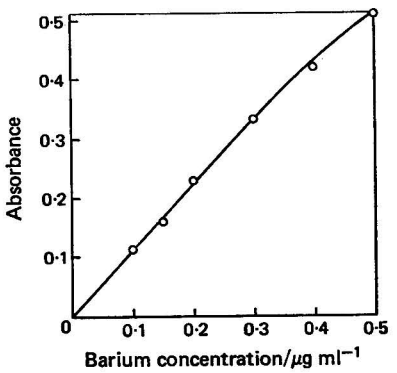

Fig. 4. Barium calibration graph. Flow-rates: argon 2·5 l min^{-1}; methane - argon (1 + 9 *V*/*V*) 0·2 l min^{-1}. 5-μl sample volume. All solutions contained 10 000 μg ml^{-1} of calcium.

The lifetime of the rod was approximately 80 firings and towards its end a gradual decrease in sensitivity was observed. The limited lifetime of the rod was thought to be due to a reaction occurring between the calcium matrix and the graphite.

The authors thank the Directors of Shandon Southern Instruments Limited for permission to publish this work.

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Received *October 18th*, 1974
Accepted *November 11th*, 1974

Analyst, March, 1975, Vol. 100, pp. 203–212

The Formation of Molybdosilicic Acids from Mixed Solutions of Molybdate and Silicate

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A fundamental re-appraisal of the conditions leading to the formation of α- and β-molybdosilicic acids has been made. The classification of these conditions recommended by Strickland has been rejected and replaced with the rigorous system involving pH and molybdate concentration in the reaction mixtures. The α-molybdosilicic acid is formed at pH between 3·8 and 4·8 (possibly slightly higher) and the β-acid at pH between 1·0 and 1·8. The yield of both α- and β-acids (at pH 4·0 and 1·2) is independent of molybdate concentrations between 0·015 and 0·100 mol l^{-1}. The rate of formation of each compound at various known pH and molybdate concentrations is discussed. A number of hitherto unexplained complications reported by other workers are now resolved.

An adequate knowledge of the conditions required for formation of molybdosilicic acid is a prerequisite of studies in all branches of molybdate - silicate chemistry, including analytical work with silicates. During studies of the behaviour of analytical methods for determining silicate in natural fresh waters, we found that the literature dealing with the conditions for molybdosilicic acid formation is confusing and often misleading. In order to overcome this confusion we have re-investigated the chemistry involved. This paper describes the results of our investigations.

The fact that molybdate and silicate species combine to form molybdosilicic acid has been used as the basis of most colorimetric methods for silicate determination. Strickland,[1] in three papers, appears to have been the first to show that there are two possible forms of molybdosilicic acid, which he termed α- and β-molybdosilicic acids. He advanced the theory that the critical factor that determines the form produced in any mixture is the ratio of the concentrations of acid and molybdate used. He stated clearly that using up to 1·5 equiv of hydrochloric acid per gram ion of molybdate (MoO_4^{2-}) produces the α-acid, while ratios above 2·0 equiv of acid per gram ion of molybdate yield the β-acid.

Since 1952 a variety of analytical methods[2–19] that are dependent upon these alternative conditions have been described, and in most instances mention has been made of Strickland's work. Although some workers[8–13] have quoted Strickland's conclusions correctly, others[14–16] have quoted him as having reported that pH is the critical factor that determines production of either α- or β-molybdosilicic acid. However, while adopting pH none of this latter group of workers has questioned the validity of their change in nomenclature.

A further group[2–7] of workers has compromised with respect to both viewpoints by using pH for one form, and acid to molybdate ratios for the other. Govett[17] seems to have been alone, until now, in recognising that these three opinions exist by default. As implied above, such anomalies are misleading and need to be rationalised. After conducting our investigations we conclude that the chaotic state of the literature on these analytical silicate procedures is due, firstly, to the fact that Strickland[1] introduced the fallacious concept of acid to molybdate ratios, and secondly, to the non-critical use of this term by subsequent workers[2–16] in this field.

Experimental

Apparatus

Whenever possible, solutions were dispensed by means of Zipette syringe pipettes (5–25 ml) or Eppendorf pipettes (0-1 ml). Tests showed that their precision is as good as grade "A" standard glassware. Thus, although reaction mixtures were not made up to a final fixed volume any variation in the total volume was negligible. Polypropylene reaction vessels (125 ml) were used throughout.

Absorbance was measured by means of a Hilger and Watts Uvichem 1600 spectrophotometer and absorption spectra were obtained by using a Unicam SP800 scanning spectrophotometer. A Metrohm E-488 pH meter, standardised with Soloid (pH 4·0) buffer tablets (Burroughs Wellcome), was used. No correction has been made for differences in ionic strength between standard and other solutions. AnalaR reagents were used throughout.

Method

The investigation of the chemistry of mixtures of silicate and molybdate was performed in a manner similar to that described by Strickland.[1] The yellow molybdosilicic acids were formed at room temperature by mixing molybdate solution (0·25 M with respect to molybdenum) with acetate buffer (if used), distilled water and mineral acid, and then adding to 45·0 ml of this mixture 2·0 ml of standard silicate solution (usually $1{\cdot}8 \times 10^{-3}$ M with respect to silicon). The acetate buffer is required in the automatic analytical method that relies upon the α-acid and that was developed as a result of this work. Unless stated otherwise, 5·0 ml of a stock solution (1·0 M with respect to both acetic acid and sodium acetate) were used when α-molybdosilicic acid was required.

The molybdate stock solution was prepared by dissolving 44·1 g l^{-1} of ammonium paramolybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in distilled water. Before use it was filtered through a Millipore membrane filter (0·8 μm average pore diameter) and stored in a polythene vessel. The standard silicate solution was prepared by fusing 1·000 g of silica (SiO_2) with 5·0 g of sodium carbonate, dissolving the cooled melt in distilled water and diluting the solution to 1 l. The stock solution was stored in a polythene vessel and aliquots diluted with distilled water to give working solutions. The absorbance of the yellow solutions was measured at 390 nm. The blue, reduced molybdosilicic acids were prepared by adding tin(II) chloride solution (1·0 ml of 0·10 N solution in 0·56 N hydrochloric acid) to a mixture of 25 ml of the yellow molybdosilicic acid solution and 24 ml of an acid - molybdate solution, which had been allowed to stand for 3 min. Strickland has shown that the hydrochloric acid (2 N) in this acid - molybdate solution is needed in order to prevent reduction of residual molybdate present in the reaction mixture. He recommended adding molybdate (0·02 M) to this solution, presumably in order to eliminate a change in the molybdate concentration of the reaction mixture during addition of the acid - molybdate solution. Although we have found the extra molybdate to be unnecessary, it was used in the work described here. Unless stated otherwise, all results have been corrected for blank solutions.

Results

Preliminary studies showed that Strickland's classification of the conditions that lead to production of α- and β-molybdosilicic acids did not operate successfully in our hands. We obtained the same product, β-molybdosilicic acid, when solutions with acid to molybdate ratios of between 0·5:1 and 4·5:1 were used; the shapes of the absorption spectra of the blue reduced molybdosilicic acids were identical. A thorough examination of Strickland's classification has therefore been made in order to understand the reasons for its failure. Our results show that the fallacious acid to molybdate ratio parameter used by Strickland should be abandoned. Instead, we recommend that a more rigorous description of the reaction conditions, which includes the pH and the concentration of molybdate in the reaction mixture, should be adopted.

Superficially, the classification used by Strickland might seem to be similar to that used here. This is perhaps not surprising because, in essence, both classifications are concerned with the importance of acid and molybdate concentration in the formation of molybdosilicic acid. However, it is important to appreciate that the two approaches are fundamentally different. Here, the two variables are considered to be independent and are treated separately; initially, Strickland adopted the same course. Thus, he studied the effects of acidity changes upon molybdosilicic acid formation at constant molybdate concentration (either $2{\cdot}7 \times 10^{-2}$ M or $3{\cdot}685 \times 10^{-2}$ M). (He did not study the effect of molybdate concentration changes at constant acidity.) Finally, however, Strickland combined the variables in the acid to molybdate ratio. A point of principle at issue here, therefore, is whether the variables can be combined in this way. Notwithstanding this aspect, there is the additional question of the

appropriateness of the acidity term used by Strickland. Thus, we have used pH where he used an amount of acid added.

It is surprising that the validity of the acid to molybdate ratio was not challenged earlier. After all, the combination of these two independent variables in such a succinct function implies a relationship that ought to have demanded an explanation in terms of the chemistry of the system. In fact, to date no workers have thought it to be remarkable that this function could be applied over the entire range of acid and molybdate concentrations. The suggestion that the ratio can define the entire reaction system implies one of two propositions. Firstly, that changes brought about by reducing one variable are exactly compensated for by reducing the other variable by the same factor. Secondly, that the reaction system is unaffected by one of the variables, and therefore that the ratio is simply a scale for the other variable. As can be seen from our results the second case applies here. Over the narrow molybdate concentration range studied by Strickland the amount and type of the product of the reaction is independent of molybdate concentration; his acid to molybdate ratio scale was therefore an acidity scale.

The ultimate test of the validity of the acid to molybdate ratio classification is that all solutions with the same ratio should have the same pH. Strickland's own results suggest that this is not so. He did not obtain identical curves when he titrated his $2{\cdot}7 \times 10^{-2}$ M and $3{\cdot}685 \times 10^{-2}$ M molybdate solutions with hydrochloric acid. We have substantiated this observation by measuring the changes in pH that arise during successive dilutions of solutions at constant acid to molybdate ratio. The results (Fig. 1) show that solutions of constant acid to molybdate ratio can span a wide range of pH values. Therefore, the proportions of α- and β-molybdosilicic acids formed in reaction mixtures with constant acid to molybdate ratio can vary.

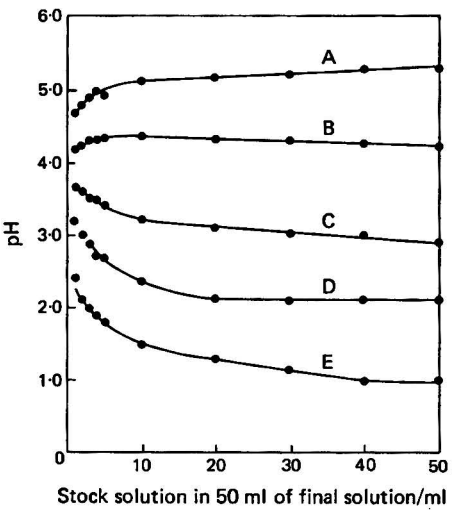

Fig. 1. Effect of dilution on the pH of solutions with constant acid to molybdate ratio. Various known amounts of stock solution (containing 0·125 M molybdate-molybdenum and hydrochloric acid) were diluted to 50 ml with distilled water. Acid to molybdate ratio: A, 0; B, 0·76; C, 1·32; D, 1·56; and E, 3·60.

When describing the formation of α- and β-molybdosilicic acids, Strickland discussed acid to molybdate ratios as well as the pH of the reaction mixtures. Illogically, however, he chose to describe the acidity of the mixtures in terms of the amount of hydrochloric acid that he added to the arbitrarily chosen molybdate solution that he started with. Although he presented titration curves for his molybdate solution he seems to have been unaware

that the origin of the curves (0 equiv of acid, pH 5·7?) is of limited significance and relates only to his molybdate solution. Therefore, both Strickland and subsequent workers who have used the acid to molybdate ratio have not realised that this classification is susceptible to the presence of unsuspected alkalinity or acidity in one, or all, of the reagents. Additional alkalinity in the reagents increases the acid to molybdate ratio that is required to produce a given pH for the reaction mixture. The magnitude of this effect can be seen by comparing the alkalinities of the molybdate reagents used in this work with those used by Strickland.[1] First, it is necessary to calculate the alkalinity of his molybdate solution. We can write

Alkalinity of molybdate solution + alkalinity of standard silicate solution
≡ acid used to lower the pH to a given value

With Strickland's results, therefore,

5 ml of x N hydroxide + 2 ml of $1{\cdot}20 \times 10^{-1}$ N hydroxide
≡ y (5 ml of 0·27 M molybdate-molybdenum)

where x is the unknown molybdate alkalinity factor (expressed as a hydroxide equivalent) and y is the acid to molybdate ratio. Although y can have several values we have adopted values of 1·5 and 2·0. According to Strickland's results these correspond to the production of α-molybdosilicic acid at a pH of 3·8 and β-molybdosilicic acid at a pH of 2·0, respectively. The alkalinity factor ($1{\cdot}20 \times 10^{-1}$) associated with the silicate standard has been incorporated because Strickland used a $5{\cdot}0 \times 10^{-3}$ M solution of alkali-degraded α-molybdosilicic acid. (A solution of solid α-molybdosilicic acid was degraded by adding 24 equiv of alkali per mole of α-molybdosilicic acid.)

The use of the above equation gives Strickland's molybdate alkalinity factor the values of 0·357 and 0·492, for α- and β-molybdosilicic acids, respectively. These values should be compared with the much lower alkalinities of 0·060 (pH 3·8) and 0·150 (to pH 2·0) obtained by direct titration of our ammonium molybdate with hydrochloric acid. An alternative way of comparing these two sets of results is to examine the acid to molybdate ratios that they represent. The appropriate acid to molybdate ratios for our solutions can be obtained by using the equation in reverse, that is, by substituting our alkalinity values into the titration equation. By this means, we found that if Strickland had used our ammonium paramolybdate solution, the acid to molybdate ratios required for the formation of α- and β-molybdosilicic acids would have been 0·40 and 0·73, respectively, instead of his reported values of 1·5 and 2·0.

An examination of the variety of methods that have been recommended for reagent preparation shows that significant variation in alkalinity is very likely to occur. Standard silicate solutions contain different amounts of residual carbonate; Strickland and Parsons[10] recommend the use of either potassium fluorosilicate or a silicate solution prepared by carbonate fusion. Molybdate solutions have been prepared from sodium molybdate, ammonium molybdate, ammonium paramolybdate or by carbonate fusion of molybdenum(VI) oxide. As these solutions almost certainly possess different alkalinities, and as Strickland's[1] approach is susceptible to such differences, it is not surprising that the classification based on acid to molybdate ratio is not universally applicable.

Variation of pH at Constant Molybdate Concentration

Information about the size of the pH range that leads to the formation of α- and β-molybdosilicic acids is required before an analytical method can be assembled. We conducted several sets of experiments in order to obtain such information and the results of two of them, which are representative of the remainder, are discussed below. The experiments were conducted by the method described above; the acetate buffer was not included. In one experiment the variation of the absorbance of yellow molybdosilicic acid, produced at various known pH levels, was studied. In the other, the absorption spectra at 450–850 nm of 13 solutions of molybdenum blue derived from a set of solutions of the yellow molybdosilicic acids were allowed to develop until their absorbances attained a steady value (changes of less than 0·002 in 10 min). Exceptions were made at extreme pH values where the rate of formation of the yellow molybdosilicic acids is very low and complete formation takes too long (Table I). In these instances a maximum reaction period of 30 min was allowed. It would have been most convenient to have been able to allow a standard reaction time, of say 30 min, in which

the absorbance of all of the molybdosilicic acid solutions could have attained a maximum value. However, the transformation of the formed β-acid into the α-acid precludes this possibility and a variable reaction time has to be adopted.

TABLE I

APPROXIMATE TIME REQUIRED TO ATTAIN MAXIMUM ABSORBANCE (390 nm) AT VARIOUS pH VALUES

Silicate-silicon, 2 mg l^{-1}; molybdate-molybdenum, $2{\cdot}5 \times 10^{-2}$M.

pH	1·0	1·2	1·4	1·6–3·0	3·8–4·2	4·4	4·6	4·8	4·9
Time/min ..	30	15	10	7	10	12	14	20	30

Both sets of results (Fig. 2) show that two pH ranges are of immediate interest: one between 1·0 and 1·8 for β-acid formation and the other between 3·8 and 4·8 for α-acid formation. pH values outside or between these two ranges are of little direct interest to the analyst, as either the reactions are too slow or mixtures of α- and β-molybdosilicic acids are formed. With the yellow solutions interpretation of the results is concentrated only on the plateau regions of the graph. The position of these plateaux relative to the ordinate axis depends

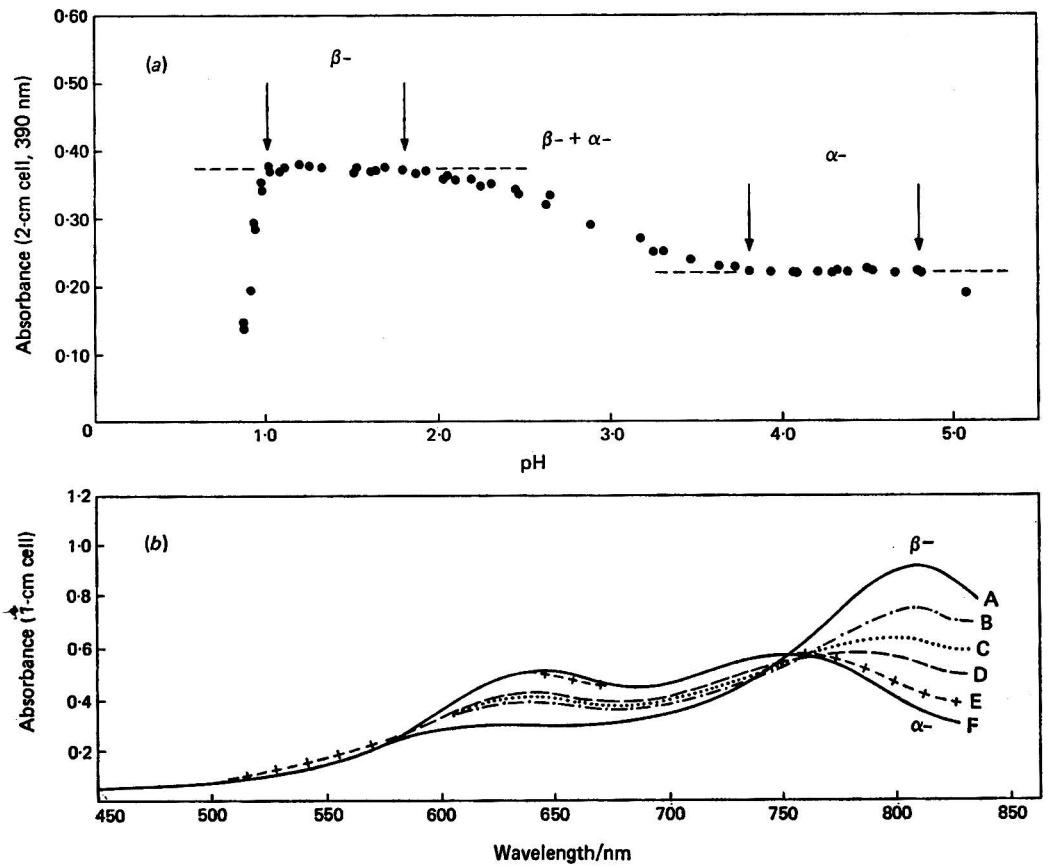

Fig. 2. (*a*), Absorbance of yellow molybdosilicic acid solutions formed at various pHs (composition of mixture: 2 mg l^{-1} silicate-silicon, $2{\cdot}5 \times 10^{-2}$ M molybdate-molybdenum). Reaction period ⩽ 30 min, temperature 20 °C. (*b*), Absorption spectra of solutions of molybdenum blue obtained by reduction of yellow molybdosilicic acid solutions similar to those in (*a*). Reduction accomplished using tin(II) chloride. pH of yellow solution prior to its reduction: A, 1·0–1·8; B, 2·4; C, 2·8; D, 3·0; E, 3·3; and F, 3·8–4·8.

on the wavelength at which the absorbance is measured. From the results of other work[15,20] it can be seen that the specific extinction of α-molybdosilicic acid can equal (approx. 330 nm) or even exceed that of the β-acid (below 330 nm). Thus, had the absorbance of the yellow solutions been measured at approximately 330 nm, little or no differentiation of α- and β-forms would have been possible by this method.[20] At wavelengths shorter than 330 nm the plateau for α-molybdosilicic acid would have been located at a higher position than that for β-molybdosilicic acid. Interpretation of the absorption spectra of the blue derivatives is concentrated on the extreme instances, the region between which corresponds to the mixtures of α- and β-molybdosilicic acids. Thus, for five regularly spaced pH levels between 3·8 and 4·8 the absorption spectra were coincident. Similarly, pH levels between 1·0 and 1·8 produced a second group of coincident spectra.

The pH range for α-molybdosilicic acid is much wider than some workers have reported.[1,2,17] Indeed, in most instances their graphs of absorbance *versus* pH show little evidence of an α-molybdosilicic acid plateau region. It seems likely that the arbitrary reaction period (not more than 10 min) used by Strickland,[1] Morrisson and Wilson[2] and Govett[17] was too short, and that the development of the α-acid was truncated. Nevertheless, the pH range for α-molybdosilicic acid reported here is considerably narrower than that obtained by some other workers[15,18] who have adopted higher temperatures. At higher temperatures the transformation of the β-acid into the α-acid is enhanced, and it is possible to extend the pH values for α-acid production across the whole range between pH 1·0 and 4·8. We have not investigated this possibility because we wished to design analytical procedures that did not incorporate any heating operation. This constraint was applied because our experience suggests that automatic procedures using the Technicon AutoAnalyzer operate more precisely when heating coils are avoided. Nevertheless, the observation emphasises that the size of the pH ranges for α- and β-molybdosilicic acid production are temperature dependent.

Variation of Molybdate Concentration at Constant pH

Previously, little has been said about the effects of large changes in molybdate concentration of reaction mixtures. We have therefore studied the effects of imposing a 50-fold change in the molybdate concentration used in the reaction mixtures. The experimental procedure described above was used; the acetate buffer was included in the reaction mixtures used for α-molybdosilicic acid production and if necessary the pH was adjusted with hydrochloric acid. Various known amounts (0·5–25 ml) of 0·25 M molybdate-molybdenum solution were used in place of the 5 ml recommended by Strickland. Concomitant changes in the distilled water contribution were made to maintain the total volume constant (45·0 ml). The pH of the mixtures were within 1·20–1·40 for β-acid formation, and 4·05–4·29 for α-acid formation. The β-acid solutions were allowed to stand for between 5 and 20 min before measurement, while 90 min were allowed for α-acid solutions.

In both instances the corrections for blank solution (0 μg l^{-1} of silicate-silicon) increased with increased amounts of molybdate. Nevertheless, after correcting for the blanks, the results showed that the yield of the α-acid was the same with between 0·005 and 0·100 mol l^{-1} of molybdate-molybdenum present in the final mixture. The absorbance measurements (at 390 nm, 4-cm cell and 2 mg l^{-1} of silicate-silicon) ranged between 0·423 and 0·412. However, with 0·0025 mol l^{-1} of molybdate-molybdenum the yield dropped to 89 per cent. of this value. The yield of the β-acid was constant with between 0·015 and 0·100 mol l^{-1} of molybdate-molybdenum present. The absorbance measurements (390 nm, 2-cm cell, 2 mg l^{-1} of silicate-silicon) ranged between 0·353 and 0·362. However, with between 0·0025 and 0·015 mol l^{-1} the yield of the β-acid was heavily dependent upon the molybdate concentration. A further experiment showed that the reaction was relatively slow in the mixture containing 0·010 mol l^{-1} of molybdate-molybdenum, and that at least 70 min were required for the absorbance to stabilise. The discrepancy between the yield of the β-acid in this mixture and those containing the higher concentrations of molybdate was reduced to 4 per cent. when a stable absorbance had been reached (1·5 h). The results show, therefore, that a molybdate concentration similar to that used by Strickland[1] is satisfactory for an analytical procedure.

It is interesting to note that the acid to molybdate ratios of the β-acid solutions described above ranged from 0·48 to 24·0 (equivalents of acid to moles of molybdate). According to

Strickland's classification, therefore, both the α- and β-acids should have been formed. However, the four solutions that produced maximum yields of the β-acid had ratios between 0·48 and 1·3 and were therefore apparently appropriate to α-acid formation. Further, five solutions that did not yield the maximum amount of the β-acid had ratios between 4·8 and 24·0, apparently appropriate for β-acid formation. These results are therefore in total conflict with Strickland's[1] classification, and show unequivocally the inadequacy of the acid to molybdate ratio concept.

Hitherto Unexplained Complications

Govett,[17] in 1960, found that unless the pH of the stock molybdate solution (0·2 to 0·5 M with respect to molybdenum) was kept above about 7·0, the reproducibility of the analytical method was poor. He states that this effect is enhanced when molybdate solutions are more than 12 h old, but that stock solutions at a pH above 7·0 are stable for at least 1 week. Further, he reports that with untreated molybdate solution, the yield of molybdosilicic acid depends on the order in which the reagents are mixed. As we wished to exclude problems of this kind, we examined Govett's[17] work in detail. Our results suggest that he was mistaken in his belief that molybdate solutions below pH 7·0 deteriorate in this way. Our investigations suggest that Govett's[17] problems were due to incipient α-acid formation in his β- and α-acid mixtures.

In the first series of experiments, we tested the effect of storing 0·25 M ammonium molybdate solutions of various acidities for 42 h. We found that the reproducibility and yield of both α- and β-acid methods was unaffected when acidified molybdate was used instead of untreated ammonium molybdate (Table II). The experiments were performed by suspending the analytical procedure at various stages for the 42-h period. Thus for β-acid formation, aliquots of acidified molybdate, prepared by mixing acid and molybdate reagents, were stored. Aliquots of untreated molybdate were held until complete analysis was performed. In this way, the introduction of additional reagents was avoided.

TABLE II

EFFECT UPON MOLYBDOSILICIC ACID FORMATION OF SUBSTITUTING ACIDIFIED MOLYBDATE FOR AN UNTREATED SOLUTION

Approximately 2 mg l^{-1} of silicate-silicon.

	Mixture	Storage time/h	No. of samples	Absorbance at 390 nm (2-cm cells)	Standard deviation
α-Molybdosilicic acid	Molybdate only, pH 5·6	0	5	0·233	0·001
	Molybdate + acid, pH 4·5	42	9	0·230	0·001
	Molybdate + acid + water, pH 4·5	42	9	0·232	0·001
β-Molybdosilicic acid	Molybdate only, pH 5·6	0	9	0·418	0·002
	Molybdate + acid, pH 0·8	42	9	0·418	0·001

Another set of tests was conducted to investigate the effect of changing the order in which reagents are added. The results confirmed our expectation that reagent order would be important only with a β-acid procedure. This is understandable, because in an α-acid procedure, the pH of any combination of reagents is always higher than the required pH and only α-molybdosilicic acid can form. However, as pointed out by Strickland and Parsons, when a β-acid is prepared it is essential to guard against incipient α-acid formation, which can occur in any mixture of molybdate and silicate with a pH of approximately 5. In tests of this behaviour we found that our solutions of the β-acid returned an absorbance of 0·431. The comparable α- and β-acid mixture, produced by allowing incipient α-acid formation to take place at pH 5·6 for 4 min, returned a value of 0·378. The magnitude of the error is therefore relatively large for only a short time of reaction at a high pH.

In our experiments the timing was precise, but if, as is likely to occur in manual procedures, timing is not as precise, poor reproducibility will result. Strickland and Parsons overcame this problem by adding the silicate sample to the mixture of acid and molybdate. One can also understand why Govett's empirical approach of adding alkali to his molybdate stock solution improved the reproducibility of his procedure. It eliminated the incipient α-acid formation that would have occurred.

Both Strickland[1] and Govett[17] reported that the yield of molybdosilicic acid was different when sulphuric acid was substituted for hydrochloric acid. Strickland[1] only observed the difference when the β-acid was formed. In contrast, Govett[17] reported that the results for sulphuric acid were consistently higher in all mixtures. When Strickland's[1] results are interpreted in terms of pH instead of acid to molybdate ratio, the discrepancies between the two sets of results disappear. Close inspection of Govett's results[17] also supports the contention that there is no real difference between the two sets of results as the maximum differences amount to 2 per cent. of the total yield; an increment possibly within the error of such an experiment. An exception to this was observed with solutions the pH of which was less than 1·0. However, in these solutions the yield of the β-acid is critically dependent upon both the time allowed for reaction and the precise pH of the solution. In view of this fact we were not surprised to find that Govett[17] observed differences as large as 10 per cent.

Because of these uncertainties we investigated the yield of both α- and β-acids in solutions containing hydrochloric, sulphuric or nitric acid. The solutions of the α-acid contained 5×10^{-2} equiv l^{-1} of mineral acid, which was required in order to lower the pH to the desired level (4·0) when the acetate buffer, molybdate and water had been mixed. The solutions of the β-acid contained 0·1 equiv l^{-1} of acid and the pH of these solutions was 1·5. In each instance, all reagents, except the acid and standard silicate solution, were dispensed from a bulked solution, thereby reducing the number of dispensing errors. After preparation, and before the absorbances were measured, all the yellow solutions were randomised. A set of blank solutions was treated in the same manner. The solutions of the α-acid were developed for 1 h and the β-acid solutions for between 10 and 30 min.

With both α- and β-acids, the statistical Bartlett test showed that the variances obtained with the three mineral acids did not differ significantly at the 5 per cent. level. Therefore, the reproducibility of the procedure was not dependent upon the type of acid used. Further, the statistical *t*-test of the means of the groups showed that they were not significantly different at the 1 per cent. level. The results (Table III) show, therefore, that any of the three mineral acids can be used for developing the yellow compounds. Additional tests showed that nitric acid at this concentration interferes with the reduction of molybdosilicic acid by tin(II) chloride. Therefore, the use of nitric acid should be restricted to procedures that rely only upon the yellow molybdosilicic acid.

TABLE III

EFFECT OF CHANGING ACID USED IN PREPARATION OF MOLYBDOSILICIC ACID

Eight samples tested in each instance; approximately 2 mg l^{-1} of silicate-silicon.

	Absorbance of α-compound at 390 nm (4-cm cells)			Absorbance of β-compound at 390 nm (2-cm cells)		
	HCl	HNO_3	H_2SO_4	HCl	HNO_3	H_2SO_4
Mean value with silicate	0·513	0·522	0·512	0·448	0·455	0·446
Mean value without silicate	0·051	0·061	0·052	0·061	0·070	0·062
Increment	0·462	0·461	0·460	0·387	0·385	0·384
Standard deviation of increment × 10^3 (eight samples)	2·8	3·4	3·9	2·6	2·0	2·8

Tests that showed that the product of the reaction at pH 4·0 is not changed significantly by the presence of acetate and acetic acid were also conducted. The absorption spectra of the blue reduced products derived from two solutions, one with acetate buffer and the other without, were examined, absorbance being measured at 10-nm intervals. Between 430 and 750 nm the maximum and mean differences (sign neglected) were 3·4 and 1·2 per cent., respectively. (The mean, with the sign included, was 0·5 per cent.) Between 750 and 850 nm the maximum and mean differences were 6·7 and 4·5 per cent., respectively. In this latter instance all the absorbances for the acetate-derived solution were higher than those for the other solution. Nevertheless, in each instance differences of this magnitude are unlikely to be significant.

The Transformation of β- into α-Molybdosilicic Acid

The mechanism by which α-molybdosilicic acid is formed at a pH above 3·8 is in dispute. Strickland and subsequent authors have pointed out that the α-acid might form either

directly, or via β-molybdosilicic acid. The latter mechanism was prompted by the observation that the β-acid is transformed into the α-acid at lower pH values. The results of our preliminary investigations show that of the two, the former mechanism is the more likely.

In our experiments, the pH of solutions of β-molybdosilicic acid, formed in 10 min from molybdate and silicate in the manner mentioned previously, was increased rapidly from 1·2 to 4·2 by the injection of 6 ml of acetate buffer (1 M in both acetic acid and sodium acetate) into 25 ml of β-molybdosilicic acid solution. The behaviour of the transformation reaction in these solutions was compared with the behaviour of the formation reaction of α-molybdosilicic acid from silicate and molybdate in mixtures of the same composition. We found that transformation was much slower than direct formation. In solutions containing 2 mg l^{-1} of silicon, transformation required at least 1·5 h, whereas direct formation required only 11 min. It was also found that the transformation rate decreases with decreasing concentration of β-molybdosilicic acid. Initial rates of change in absorbance (2-cm cells, 390 nm) in solutions containing 6·0, 4·0 and 2·0 mg l^{-1} of silicon were 27×10^{-3}, 17×10^{-3} and 7×10^{-3} per min, respectively; the initial absorbances were 0·89, 0·60 and 0·30, respectively. An extrapolation of these initial rates to the low concentrations of β-molybdosilicic acid, which have been presumed to exist transiently during formation of the α-acid, produces a rate of reaction too low to account for the observed rate of α-acid formation. It seems, therefore, that transformation cannot precede formation.

Discussion

The conditions that lead to production of either α- or β-molybdosilicic acid have been described. At present, we feel that the only satisfactory definition of α- and β-acids is an operational one, involving the pH and concentration of the molybdate in the reaction mixtures used. Although it is true that a solid, so-called, α-molybdosilicic acid can be prepared,[1,21] we feel that there are two overriding reasons why the operational definition is preferable at this time. Firstly, a solid β-molybdosilicic acid that is comparable with the α-acid has not yet been isolated. Secondly, there is little or no evidence that the solid α-acid is in fact the same material as that formed in solution. During preparation, the solid is extracted from aqueous solution with diethyl ether. It is conceivable, therefore, that changes might occur at that stage.

Liss and Spencer[9] seem to have been the only workers to attempt a satisfactory comparison of both solid and solution derived forms. Unfortunately, they were confused by the acid to molybdate ratio concept, and, as a result, used the conditions (pH 3·6) of the Grasshoff[16] sea-water silicate method. At this pH their solutions of molybdosilicic acid might have been α- and β-acid mixtures; it is not surprising, therefore, to find that a discrepancy existed between the α- and β-acid mixtures and the solutions of the solid preparation. Nevertheless, according to our results the 15 per cent. discrepancy that they record seems to be too large to be due entirely to this single factor. It seems possible that solid- and solution-derived molybdosilicic acids might differ slightly, although the additional ionic strength resulting from the use of sea water might also be responsible.

Thanks are due to Mr. A. G. P. Debney for his encouragement and to the Director of the Institute of Hydrology for permission to publish this paper.

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Received *June 3rd*, 1974
Accepted *October 2nd*, 1974

Book Reviews

ADVANCES IN NUCLEAR QUADRUPOLE RESONANCE. Volume 1. PAPERS PRESENTED AT THE INTERNATIONAL SYMPOSIUM ON NUCLEAR QUADRUPOLE RESONANCE, SEPTEMBER 28–29, 1972. QUEEN ELIZABETH COLLEGE, UNIVERSITY OF LONDON, ENGLAND. Edited by J. A. S. SMITH. Pp. xviii + 434. London, New York and Rheine: Heyden. 1974. Price £14·50; $39·50; DM119.

Nuclear quadrupole resonance spectroscopy is still happily at that state of development at which most chemists can follow and appreciate current developments. It has not yet enshrouded itself in its own private nomenclature, designed to obscure rather than to reveal, known only to the cognoscenti, which would make it difficult for the ordinary analyst or chemist to appreciate new work and thus make him dependent upon some expert. This branch of spectroscopy is still accessible and comprehensible to those who are prepared to master the simple basic principles of the technique. It is true that nuclear quadrupole resonance has been a long time growing. The first results of chemical significance were published more than twenty years ago, and theories for the treatment of data have been available for about the same length of time. The effect is quite a delicate one and it would appear to have required until now for adequate instruments to be developed. This first volume of "Advances in Nuclear Quadrupole Resonance" therefore appears at a particularly apposite time. It is the collection of papers presented at an international conference held at Queen Elizabeth College in 1972. It covers all aspects of nuclear quadrupole resonance with particular emphasis on modern instrumental advances. Super-regenerative oscillators are described in detail and the advantages of a pulsed nuclear quadrupole resonance spectrometer are discussed. Chlorine and other halogen resonances are, of course, described in the greatest detail. Various papers demonstrate the value of nuclear quadrupole resonance, not only in investigating local charge distributions involving p orbitals, but also as a probe for details of molecular structure and as a means of studying inter-molecular effects. Particularly interesting are the few papers that deal with deuterium and nitrogen-14 nuclear quadrupole resonance studies. These are difficult experimentally because of the relatively low frequencies involved but the application of nuclear quadrupole resonance promises results that will be of very great significance in both chemistry and biochemistry.

The greatest interest in nuclear quadrupole resonance is amongst those chemists who hope that it will provide them with greater insight into the chemical bond. But the potential for analysis has in no way been ignored. A long, detailed and interesting paper by Fitzky shows how nuclear quadrupole resonance data can be used analytically. Chlorine bound to different elements (Cl—X) will give resonant frequencies in different characteristic ranges, enabling the chemical nature of X to be determined. Rather more important is the use of the pattern of observed resonance frequencies (which can be determined with a precision of 1 in 10^6) to identify unequivocally particular chlorinated species; even isomers give quite different and distinct spectra. Valuable information that can aid in structural determinations can also be obtained.

This book is handsomely produced and provides the chemist and the analyst, and not just the nuclear quadrupole resonance specialist, with a detailed and understandable account of current progress and achievements in this field. Heyden are to be congratulated on the quality of this book, which, like the price, is very high. I have just one regret, however, that no means was found (picture on the dust cover, or a miniature record) to convey that most memorable moment of the conference dinner, the triumphant entry, bugles blowing, drums banging, of the Grenadier Guards!

D. S. URCH

MODERN MICROSCOPY. ELEMENTARY THEORY AND PRACTICE. By C. F. A. CULLING. Pp. xii + 148. London: Butterworths. 1974. Price £1·50.

"Modern Microscopy," a soft covered book, has been written to fulfil the need for "a complete, yet concise, practical text-book on the subject." The author has had twenty years' experience in teaching microscopy and, as he rightly states, there is a lack of knowledge on the use of the instrument. The aims of the book are clear and the need undoubtedly established but, unfortunately, this book does not fill the gap.

The title of the book is all-embracing but many aspects of modern microscopy, *e.g.*, the whole of reflected light microscopy, is omitted. For the sake of completeness, a brief chapter on the electron microscope is included at the end, but the author is faced with an impossible task; the subject just cannot be covered, even in an elementary fashion, in one chapter. Scanning electron

microscopy is omitted. The contents of the book are devoted entirely to biological applications and almost a quarter of it specifically to fluorescence microscopy. It is on this subject where the author is clearly dealing with his own speciality, and the subject is well covered, although the instrument itself is referred to as a "fluorescent microscope."

In order to make the underlying optical theory readily understood there are many over-simplifications, which I often found more difficult to follow than more rigorous explanations. Many instances of this criticism could be quoted, *e.g.*, in the chapter on polarised light microscopy we have "Light is assumed to be due to a wave motion, to the upward and downward vibration of ether particles" and the next but one sentence "Ether is supposedly an homogeneous medium and there is no reason therefore to believe that these particles will vibrate in any direction more than another." The polarised light chapter also suffers from confusion between optical activity and birefringence in crystals, with the result that neither is properly explained and students reading it would pick up many erroneous ideas. The explanation of phase contrast microscopy is in simple language but not easy to follow. This subject has been dealt with lucidly and quite rigorously, yet in a suitable manner for students, in at least one other text-book ("The Use of the Microscope," by R. Barer, Laboratory Aids Series, published by Blackwell).

It is not only in the more complicated microscope sections that errors occur. The first two sentences of the chapter on photomicrography state that "Microphotography is the process of taking minute photographs. Photomicrography is the process of taking photographs through a microscope, and it is surprising how often the former term is used to describe the latter process." On page 16 we read "Apochromatic objectives should always be used for microphotography." Number 1 cover slips are recommended, whereas for all microscopes number 1½ most closely approach the thickness of 0·17 or 0·18 mm for which transmitted light objectives are designed. There is no discussion of objective resolution, and the factors which limit it, a subject of central importance to the high resolution microscopy of living objects. The length of the body tube for many microscopes is 160 mm, the so-called mechanical tube length, and it is measured with objective and eyepiece removed. When discussing the subject in this book, 18 mm is subtracted for the "depth of the nosepiece" (which surely can only mean the length of the objective *plus* turret) giving an actual length of tube of 142 mm. Many more similar errors could be quoted but one piece of basic advice must be contradicted. Under "daily cleaning routine" microscopists are advised to polish daily the outer surface of the objectives with lens paper or well washed silk. Objective surfaces should always be blown free of dust if possible; if a tissue is needed, the fewest number of wipes to clean the objective should be used, never polish.

It is regrettable that this book cannot be recommended to fill the very real need for which it was written.

G. D. WOODARD

INTERPRETATION OF THE INFRARED SPECTRA OF ORGANOPHOSPHORUS COMPOUNDS. By L. C. THOMAS. Pp. x + 276. London, New York and Rheine: Heyden. 1974. Price £7·50; $20·50; DM61·50.

Workers involved with the infrared spectroscopy of organophosphorus compounds will almost certainly be familiar with the published work of Thomas and Chittenden. The bulk of this book (Chapters 2 to 16) is, in the main, an extension of this work providing invaluable spectroscopic data lucidly discussed and tabulated.

The remainder (Chapter 17) contains examples of infrared spectra of a range of phosphorus compounds some, as the author admits, of doubtful purity. A detailed "blow by blow" account is given of a logical approach to the interpretation of these spectra using information from the other chapters and also from two other acknowledged sources. The amount of information that the author derives from these spectra may come as a surprise to some spectroscopists. Obviously the ready availability of nuclear magnetic resonance spectroscopy may account for this!

A real problem with this chapter is the poor layout of the spectra, which involves the reader in much page turning and neck twisting; a point that should receive the publisher's attention on reprinting. One or two errors are apparent in the references which, rightly or wrongly, makes one expect to find others. Incorrect references can be very frustrating and a further check could have been profitable.

These really are minor criticisms of an excellently written, neatly presented and modestly priced book, which I have no doubt will become the "Bellamy" of the organophosphorus chemist. I have no hesitation in recommending it and am only sorry that it did not appear 10 years earlier.

R. HARPER

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF NUCLEI OTHER THAN PROTONS. Edited by THEODORE AXENROD and GRAHAM ALAN WEBB. Pp. xiv + 407. New York, London, Sydney and Toronto: Wiley-Interscience. 1974. Price £10.

The potential value of nuclear magnetic resonance measurements on nuclei other than protons has been appreciated since the early days of nuclear magnetic resonance spectroscopy, and there has been a steady stream of publications describing such investigations. However, practical problems and instrumental difficulties have, until recently, delayed the full exploitation of important nuclei, such as carbon-13, which occur in low natural abundance and have low nuclear magnetic resonance sensitivity. Most routine measurements have therefore been concerned with protons.

The introduction of commercial pulse Fourier transform spectrometers, which through multichannel excitation produce a great increase in sensitivity, has changed the status of non-proton nuclear magnetic resonance spectroscopy dramatically and such studies now form a rapidly expanding branch of chemistry. It is reasonable to suggest that when Fourier transform instruments become less expensive, the general usefulness of carbon-13 measurements for the elucidation of the molecular structure of new compounds will rival that of proton studies. Carbon-13 nuclear magnetic resonance spectroscopy has already helped to solve many structural problems (*e.g.*, α- and β-streptomycin) that could not be resolved by proton measurements.

The present volume is based on the Proceedings of the Advanced Study Institute on the Nuclear Magnetic Resonance Spectroscopy of Nuclei Other Than Protons, held in Tirrenia (Pisa), Italy, in September, 1972, and contains the substance of twenty-five papers on recent advances in theoretical and practical aspects of the subject that were contributed by research workers from laboratories located in Canada, Germany, Israel, Italy, Portugal, Switzerland, the U.K. and the U.S.A. Each contribution has been provided with a bibliography covering the literature up to 1972.

The Proceedings include introductory reviews on the nuclear properties of non-proton nuclei, on how and why nuclei relax, on pulse and Fourier transform methods and on the theory and application of multiple resonance methods. Other contributions consider the effect of paramagnetism on the nuclear magnetic resonance spectra of non-proton nuclei, the interpretation of carbon-13 spectra of complex organic compounds and various applications involving nuclear magnetic resonance-sensitive fluorine, nitrogen, oxygen, phosphorus, silicon and metal nuclei.

An analyst will be disappointed by the lack of information on quantitative applications of the techniques described. Fluorine-19 can be studied quantitatively by continuous-wave methods in a way similar to that used for protons, but difficulties arising from the nuclear Overhauser effect in proton noise-decoupled, carbon-13 Fourier transform spectra render integration of such Fourier transform spectra almost useless; recent work, however, suggests that these difficulties will be overcome and that quantitative carbon-13 nuclear magnetic resonance spectroscopy will become a practical proposition.

The volume has few errors and provides a useful survey of the state of the subject at the end of 1972; it will interest organic and analytical chemists who wish to widen their interest in nuclear magnetic resonance spectroscopy. J. E. PAGE

EMITTANCE AND REFLECTANCE SPECTROSCOPY. Edited by H. A. ELION and D. C. STEWART. *Progress in Nuclear Energy. Series IX: Analytical Chemistry. Volume* 11. Pp. viii + 269. Oxford, New York, Toronto, Sydney and Braunschweig: Pergamon Press. 1972. Price £13·50.

The scope of the subject matter covered by the two chapters on Reflection Spectroscopy and Infra-red Emission is very wide and consequently presents considerable problems to the authors. In general, the treatments selected, although different, are both successful, each giving a theoretical treatment followed by some well selected practical examples. However, in common with many treatments of these subjects, in an effort to provide a workable simple theory of the methods described, insufficient account is taken of the problems of determining the refractive index of a thin film, and virtually no account taken of changes in refractive indexes near absorption lines, which drastically change the operation of most of the optical systems that are described. This type of treatment tends to lead experimenters to incorrect conclusions if followed in a superficial manner, but if used correctly it could be of great help to the practical worker.

Neutron spectroscopy, a relatively new technique, is well reviewed, with a concise mathematical treatment which gives readers unfamiliar with the subject a firm basis on which to build. The comparisons obtained from neutron spectroscopy, with the better known techniques of infrared

and Raman, are well chosen and show both the limitations and strengths of the various techniques. The practical aspects and general experimental problems are discussed in some detail, but the upper useful energy limit of neutron spectroscopy is not sufficiently well indicated.

Laser - Raman has now received considerable attention, as befits a technique of major importance. It is rather disappointing that a strictly classical approach to the theory should have been adopted, especially as the author goes on to indicate that the technique is well suited to biological and adsorbed samples. The possibility of modifying such samples by the formation of quasi-excited states, apart from the general heating effects of the laser beam, have therefore been ignored. However, the over-all picture of the subject is well presented, together with carefully chosen suggestions as to possible useful future applications.

The section on photon counting is not up to the standard set by the rest of the contents. It may well be that the subject matter is far more restrictive, but the arguments for and against the technique are not well reasoned. While it is true that, when only minimal light signals are available, photon counting is the best and in some extreme cases the only practical technique, for levels just above this minimum threshold other methods based on some form of modulation are only marginally inferior, and in many situations actually superior. The author gives the impression to uninformed readers that photon counting is always superior and even that it might be advantageous to reduce light fluxes in situations when there are too large, so that the technique can be used.

The chapter on the far infrared spectroscopy of minerals and inorganics is a compilation of spectral data up to 1969, and the inorganics are restricted to those relating to naturally occurring minerals. As both transmission and reflection techniques are discussed, the material is not wholly relevant to the subject of this book. A miscellany of information is presented; single crystals, thin films and powders are examined, and the uses of polarised light and low temperatures are hinted at. The difficulties in rigidly defining a far infrared region are apparent; thus many lattice vibrations lie above the "official" 200 cm^{-1} limit, some above the 300 cm^{-1} limit selected by the author, and one above 600 cm^{-1}, while, on the other hand, some molecular vibrations are found at a few tens of wavenumbers. A few analytical applications are given.

Fourier transform spectroscopy is again only partially relevant within these covers, and only a small proportion of the text deals with emittance or true reflectance studies. The author sets out to exploit some of the newer interferometer systems in the infrared fingerprint region and rightly points out their advantages in terms of enhanced signal to noise ratio and low measurement times, which facilitate emission work and kinetic studies. The technique is simply described, but some important details are omitted; there is no mention of the depletion in energy at the ends of the beam splitter range, although the effects are apparent in some of the spectra, and quantitative aspects are not discussed. Some of the applications, such as remote sensing, are specialised, and all are slanted towards instrumental capability rather than chemical significance. When instrument time is not at a premium, one feels that the considerably cheaper dispersion spectrometer is adequate in most practical situations. Some of the photographs and diagrams are of poor quality and are badly placed in the text, and one of the addresses given is no longer valid.

In general, the reviewers feel that this book does not have such a great impact on analytical chemistry as some of the earlier volumes in the series.

E. W. T. RICHARDS
T. CARTER

Erratum

JANUARY (1974) ISSUE, p. 74, line 4 from bottom: *for* "Nitrovin, per cent. $= \frac{C \times 2}{m \times 3}$" *read* "Nitrovin, per cent. $= \frac{C}{m}$"

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A Simple Reaction-rate Method for the Determination of Biuret

The phenol - hypochlorite reaction is employed for the determination of biuret in aqueous solutions. The recommended reaction-rate method is fast, simple, sensitive (0·018 A min^{-1} per micromole of biuret), accurate (to 2 per cent.) and precise (3 per cent. relative standard deviation). The useful analytical range of concentrations of biuret is $1·6 \times 10^{-5}$ to $1·3 \times 10^{-3}$ M. The effect of the phenol concentration on the reaction rate has been studied.

The effect of interfering species such as ammonium chloride, urea and cyanurate has also been investigated.

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Analyst, 1975, **100**, 168–172.

Determination of Biphenyl and 2-Phenylphenol in Citrus Fruits by Gas - Liquid Chromatography

Biphenyl and 2-phenylphenol are steam distilled from a citrus fruit homo genate into two portions of cyclohexane. An aliquot of the first extract is analysed for biphenyl by gas - liquid chromatography. Aliquots of the first and second extracts are combined and then cleaned up and concentrated by means of further extractions prior to the gas - liquid chromatographic determination of 2-phenylphenol.

GUNNEL WESTÖÖ and ARNE ANDERSSON

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Analyst, 1975, **100**, 173–177.

Spectrophotometric Determination of Thiambutosine

N-(4-Butoxyphenyl)-*N'*-(4-dimethylaminophenyl)thiourea (thiambutosine) is made to react with 2,3-dichloro-1,4-naphthoquinone in an ethanolic medium and on rendering the reaction mixture alkaline with ethanolic ammonia solution a purple colour is developed with an absorption maximum at 540 nm. A procedure based on this reaction is described for the assay of thiambutosine in micro-amounts. The method is applied to its determination in tablets. The results are in agreement with those obtained by the official method.

M. B. DEVANI, C. J. SHISHOO and HEMA J. MODY

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Analyst, 1975, **100**, 178–181.

Spectrophotometric Determination of Vanadium in Steels with o-Phenylenediamine

A simple method for the spectrophotometric determination of vanadium is described. The absorbance of the yellow colour obtained with vanadium(V) and *o*-phenylenediamine in the presence of acetic acid is measured at a wavelength of 400 nm between pH 2·5 and 3·2 and is found to obey Beer's law between concentrations of 0·5 and 10 p.p.m. of vanadium. The effect of iron, up to a level of 200 p.p.m., can be masked with fluoride ions. For steels containing less than 1 per cent. of vanadium a prior separation of iron, either by extraction into diethyl ether or by electrolysis at a mercury cathode, is advantageous. The method is found to be suitable for the determination of vanadium in high-speed steels and chromium - vanadium steels.

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Analyst, 1975, **100**, 182–185.

The Determination of Trace Amounts of Vanadium in Titanium(IV) Chloride by X-ray Fluorescence Spectrometry

A method is described for the determination of trace amounts of vanadium in titanium(IV) chloride involving pre-concentration and the use of X-ray fluorescence spectrometric techniques. The titanium(IV) chloride is added to a 40 per cent. solution of hydrofluoric acid and the mixture evaporated to a small volume. The vanadium is precipitated as the diethyldithiocarbamate complex at pH 5·0 in the presence of a co-precipitating agent, such as manganese(VII), and collected on a cellulose filter. The titanium is retained in solution by complexing it with malic acid. A lower limit of determination of 0·05 $\mu g\ g^{-1}$ of vanadium is obtained.

G. HIMSWORTH

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Analyst, 1975, **100**, 186–191.

Device for Trace Analysis for Fluorine in Reaction Tubes by Atomic-absorption Spectroscopy

An analytical method is described for the detection of trace amounts of fluorine by atomic-absorption spectroscopy. Sodium vapour is made to react with fluorine-containing compounds at temperatures of about 800 °C, and, under certain conditions, the decrease in the atomic sodium concentration gives a relative and specific value for the amount of fluorine present. The best instrument parameters for the experimental determination were measured and theoretically interpreted; 0·8 ng of fluorine was found to be the detection limit. As an example of the practical importance of this technique of trace analysis for fluorine, its application as a fluorine-specific detector in the gas chromatography of trifluoroethanol is described.

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Analyst, 1975, **100**, 192–197.

Determination of Trace Levels of Barium in Calcium Carbonate by Atomic-absorption Spectrophotometry

A sensitive atomic-absorption spectrophotometric method for the determination of trace levels of barium in calcium carbonate using a simple graphite-rod atomiser has been developed. The calcium carbonate is dissolved in nitric acid and the solution applied to the sample cavity in the graphite rod. A detection limit of 0·0045 $\mu g\ ml^{-1}$ of barium in a solution containing 10 000 $\mu g\ ml^{-1}$ of calcium was obtained on a 5-μl sample volume.

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Analyst, 1975, **100**, 198–202.

The Formation of Molybdosilicic Acids from Mixed Solutions of Molybdate and Silicate

A fundamental re-appraisal of the conditions leading to the formation of α- and β-molybdosilicic acids has been made. The classification of these conditions recommended by Strickland has been rejected and replaced with the rigorous system involving pH and molybdate concentration in the reaction mixtures. The α-molybdosilicic acid is formed at pH between 3·8 and 4·8 (possibly slightly higher) and the β-acid at pH between 1·0 and 1·8. The yield of both α- and β-acids (at pH 4·0 and 1·2) is independent of molybdate concentrations between 0·015 and 0·100 mol l^{-1}. The rate of formation of each compound at various known pH and molybdate concentrations is discussed. A number of hitherto unexplained complications reported by other workers are now resolved.

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Analyst, 1975, **100**, 203–212.

Volume 100 No 1188 Pages 145–216 March 1975

THE ANALYST

THE ANALYTICAL JOURNAL OF THE CHEMICAL SOCIETY

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ORIGINAL PAPERS

Printed by Heffers Printers Ltd, Cambridge England
Entered as Second Class at New York, USA Post Office