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Summaries of Papers in this Issue

The Determination of Trace Amounts of Platinum in Glass by Colorimetry, Spark-source Mass Spectrography and X-ray Fluorescence Spectrometry

Methods for the determination of less than 1 $\mu g\ g^{-1}$ of platinum in glass have been investigated and evaluated. The *p*-nitrosodimethylaniline colorimetric method has been adapted to enable 0·2 $\mu g\ g^{-1}$ of platinum to be determined on 2 g of sample, while the tin(II) chloride colorimetric method has been shown to be too insensitive to permit the determination of such low concentrations. Spark-source mass spectrography, while confirming the heterogeneous distribution of the platinum throughout the glass, has also been shown to be too insensitive for the direct determination of platinum in this matrix. An X-ray fluorescence procedure has been successfully developed to enable 0·5 μg of platinum in a 1-g sample of glass to be determined with a relative standard deviation of 10 per cent. The time required for the complete analysis is 3 to 4 hours.

The proposed methods depend on the pre-concentration of platinum by co-precipitation with tellurium.

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Analyst, 1971, **96**, 177–185.

Rapid Methods for the Determination of Low Concentrations of Total Sulphur in Liquids and Gases

Part I. The Determination of Total Sulphur in Light Petroleum Distillate by Reduction with Raney Nickel

Granatelli's method for the determination of sulphur in liquid hydrocarbons has been modified to permit the determination of total sulphur in purified light petroleum distillate at concentrations below 4·0 p.p.m. w/v. A mixture of propan-2-ol and water is used as the reaction solvent in a rapid method for the determination of total sulphur in light petroleum distillate in the range 0·1 to 4·0 p.p.m. w/v with a precision of ±9 per cent. of the determined value. For concentrations in the range 0·01 to 0·10 p.p.m. a more lengthy method is given, which has an absolute precision of ±0·01 p.p.m. w/v.

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Analyst, 1971, **96**, 186–193.

Rapid Methods for the Determination of Low Concentrations of Total Sulphur in Liquids and Gases

Part II. The Determination of Total Sulphur in Natural Gas and Synthesis Gases

A rapid method developed for the determination of total sulphur in light petroleum distillate is applied to the determination of total sulphur in natural gas. The sulphur compounds present in the gas are adsorbed on to a small amount of active carbon, which is then allowed to react with a suspension of Raney nickel in a propan-2-ol - water mixture and the sulphur determined as sulphide as described in Part I of this paper. An alternative procedure for the determination of total sulphur in gases containing compounds that are not reduced by Raney nickel is also described. The compounds of sulphur are adsorbed on to active carbon, desorbed into a stream of hydrogen, which then passes through a furnace at 900 °C, and the resulting hydrogen sulphide is determined as a stain on paper impregnated with lead acetate. Methods involving the use of a carbon adsorption tube give results with a precision of ±0·5 mg m^{-3} of sulphur on samples of stenched natural gas.

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Analyst, 1971, **96**, 194–200.

The Determination of Trace Amounts of Sulphide in Condensed Steam with *NN*-Diethyl-*p*-phenylenediamine

A sensitive colorimetric method has been developed for the determination of trace amounts of sulphide in condensed steam. For precise work the colour produced by *NN*-diethyl-*p*-phenylenediamine in the presence of iron (III) ions is measured spectrophotometrically covering the range 0·5 to 100 μg of sulphide-sulphur; the standard deviations at the 100 and 1·0 μg levels are about 3 and 0·08 μg, respectively. Reasonably accurate results over the range 0·5 to 25 μg of sulphide-sulphur can be obtained "on site" by a simple visual titration of a reference solution with a methylene blue solution. The *NN*-diethyl-*p*-phenylenediamine was shown to be superior to the dimethyl homologue normally used and its use does not appear to have been reported previously. Methods of sampling and the effect of sulphite are also discussed.

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Analyst, 1971, **96**, 201–208.

The Determination of Small Amounts of Cyanide in the Presence of Ferrocyanide by Distillation under Reduced Pressure

In the analysis of effluents and waters, the customary use of lead acetate to prevent the decomposition of ferrocyanide during the distillation of cyanide is not sufficiently effective when small concentrations of cyanide (about 0·1 mg l^{-1}) are to be determined. A method is described in which the decomposition of ferrocyanide can be completely prevented by distilling off the cyanide under reduced pressure in the presence of zinc acetate. The cyanide in the distillate is determined by the pyridine - pyrazolone method.

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Analyst, 1971, **96**, 209–212.

The Automated Determination of Silicon and Calcium in Portland Cement and Associated Raw Materials

The manufacture of Portland cement clinker is a continuous large scale chemical synthesis of specific compounds. The strength of the hydrated cement matrix in concrete is a function of the original clinker compound assemblage. Control of the production of the clinker compounds has to be related to the time of passage of materials through the rotary kiln and the conditions of processing. Continuous control of the major constituents is essential and knowledge of the effects of the variation of the constituents on the physical properties of the product is desirable.

Methods are described for the automated determination of calcium and silicon in Portland cement and associated raw materials with respect to the demands, scale and nature of the process.

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Analyst, 1971, **96**, 213–219.

Determination of Calcium by Radiochemical Replacement

The determination of calcium ions in solution by radiochemical replacement of silver-110 in labelled solid silver oxalate, cobalt-60 in labelled cobalt oxalate and manganese-54 in labelled manganese oxalate has been examined. A one-to-one replacement was observed with manganese oxalate. The technique can be used to determine 2·5 to 100 μmole ml^{-1} (100 to 4000 μg ml^{-1}) of calcium, and the lower limit is reduced to 16 μg ml^{-1} by using a 50 per cent. methanol solution. Magnesium interferes to only a small extent. Each determination takes less than 5 minutes, and the precision is ± 2 per cent.

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Analyst, 1971, **96**, 220–222.

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The Determination of Trace Amounts of Platinum in Glass by Colorimetry, Spark-source Mass Spectrography and X-ray Fluorescence Spectrometry

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Methods for the determination of less than 1 $\mu g\ g^{-1}$ of platinum in glass have been investigated and evaluated. The *p*-nitrosodimethylaniline colorimetric method has been adapted to enable 0·2 $\mu g\ g^{-1}$ of platinum to be determined on 2 g of sample, while the tin(II) chloride colorimetric method has been shown to be too insensitive to permit the determination of such low concentrations. Spark-source mass spectrography, while confirming the heterogeneous distribution of the platinum throughout the glass, has also been shown to be too insensitive for the direct determination of platinum in this matrix. An X-ray fluorescence procedure has been successfully developed to enable 0·5 μg of platinum in a 1-g sample of glass to be determined with a relative standard deviation of 10 per cent. The time required for the complete analysis is 3 to 4 hours.

The proposed methods depend on the pre-concentration of platinum by co-precipitation with tellurium.

A PROGRAMME to prepare high purity silicate glasses that have low light-scattering and absorption properties indicated that glasses prepared by melting the raw materials in platinum vessels were of a lower quality with respect to light attenuation than required. The transmittance of a glass is dependent on the concentration of certain trace impurities present, for example, vanadium, chromium, manganese, iron, cobalt, nickel, copper, rhodium and platinum, which absorb light in the ultraviolet, visible and near infrared regions of the spectrum.[1] The presence of metallic platinum in glass is particularly important to the over-all transmittance of light for, if the platinum particles are very small (less than the wavelength of the light used), substantial absorption of light will occur, while if the particles are larger the light will be scattered. Russell, Spangenberg and Steele[2] have recently shown that large amounts of platinum are dissolved by fusing silicate materials with a flux in platinum ware. They showed that of the fluxes investigated the greatest attack was shown by sodium carbonate and that the amount of platinum dissolved was as high as 10 mg per 4 g of glass in some instances. As the glass samples under consideration are made in some instances by the fusion of sodium and calcium carbonates with silica in platinum vessels an accurate method for determining the platinum content is necessary.

Colorimetry[3,4,5,6,7] provides the widest range of methods used for the determination of platinum, but of these only the tin(II) chloride[8] and the *p*-nitrosodimethylaniline[9] methods have been widely accepted. The tin(II) chloride method lacks sensitivity. The determination levels have been reduced with this method by taking larger samples; up to 20 g have been used.[10] This is not practical in glass analysis when 2-g samples are the maximum amounts that can be handled easily. The *p*-nitrosodimethylaniline method is susceptible to several interferences but is more sensitive. This method is stated to have an optimum range of determination of 0·7 to 2·4 $\mu g\ ml^{-1}$ of platinum in 50 ml of solution, which corresponds to the determination of 17·5 to 60 $\mu g\ g^{-1}$ of platinum in the glass, when using 2 g of sample.

Of the other techniques used for the determination of platinum, atomic-absorption spectrophotometry[11,12] and polarography[13] are too insensitive, and X-ray fluorescence[14,15] requires further investigation to be of use. Neutron-activation analysis,[16,17] while potentially satisfactory, was not investigated because the necessary equipment was not readily available and the time for analysis would, therefore, be excessive.

The aims of the present work were (*i*) to modify and improve the tin(II) chloride or *p*-nitrosodimethylaniline colorimetric methods, and (*ii*) to develop an instrumental method to simplify the analysis and reduce the analysis time.

Experimental

Reagents—

Platinum(IV) solution—Prepare a solution containing 1 000 μg ml^{-1} of platinum by dissolving the appropriate weight of chloroplatinic acid in 0·15 M hydrochloric acid, then dilute the solution as required. This solution was standardised gravimetrically by reduction with formic acid.[18]

Sodium silicate solution—Dissolve the appropriate amount of sodium silicate, Na_2O,SiO_2, in water as required.

Sodium tellurite solution—Prepare a solution containing 0·5 mg ml^{-1} of tellurium by dissolving the appropriate weight of sodium tellurite in water.

p-*Nitrosodimethylaniline solution, 0·25 per cent. w/v*—Prepare by dissolving the appropriate amount of reagent in fresh absolute ethanol.[9]

Buffer solution, pH 2·2 ± 0·2—Mix 50 ml of 4 M sodium acetate with 53 ml of 4 M hydrochloric acid.

Tin(II) chloride solution—Prepare as required by dissolving the appropriate amount of tin(II) chloride in 3·5 M hydrochloric acid.

Boric acid solution, 5 per cent. w/v—Dissolve the required amount of boric acid in water.

Apparatus—

Absorbance measurements were made with a Hilger and Watts Uvispek spectrophotometer. Spark-source mass-spectrographic work was carried out with an A.E.I. MS7 double-focusing instrument of the Mattauch - Herzog type, fitted with ion-beam chopping equipment.[19] Ilford Q2 photographic plates were used for recording the mass spectra.

X-ray fluorescence measurements were made with a Philips PW1540 total-vacuum spectrometer.

Results and discussion

Colorimetry—

Tin(II) chloride method—The method described by Ayres and Meyer[8] was followed, pure solutions of platinum and solutions containing the same amount of platinum in the presence of sodium silicate being used.

The required volume of standard platinum solution was transferred to a 100-ml calibrated flask and 10 ml of concentrated hydrochloric acid, 25 ml of 20 per cent. w/v ammonium chloride solution and 20 ml of M tin(II) chloride solution were added; the volume was then made up to 100 ml. A blank sample was prepared from the same amounts of reagents. The tin(II) - platinum(II) chloride complex formed was extracted with isopentyl acetate containing 1 per cent. of resorcinol and the absorbance measured at 410 nm with a 4-cm cell. Two series of experiments were carried out in which 10 and 15-ml portions of isopentyl acetate solution were used.

The results shown in Fig. 1 (graphs A and B) indicated that the minimum amount of platinum that can be determined with satisfactory precision by this method is 3 to 4 μg, which is a small improvement on the previous results[8] as 4-cm absorption cells were used in the present work, while Ayres and Meyer used only 1-cm cells.

In the presence of sodium silicate the platinum solutions were prepared by evaporating to dryness with 40 per cent. w/v hydrofluoric acid in PTFE beakers and dissolving the residue in hydrochloric acid. Some typical results for platinum recovery in the presence of 1 g of sodium silicate by the tin(II) chloride method are shown below.

Platinum added	0	10	20	30
Platinum recovered	0, 0	4, <4	12, <4	18, 4

It would seem from these results that either the platinum is lost during some stage of the determination or possibly that a platinum compound is formed, which is inactive in the tin(II) chloride method. As sodium silicate is soluble in water, the experiments were repeated by using water instead of hydrofluoric acid for the dissolution, and glass beakers instead of PTFE beakers to check if platinum is lost with the dissolution technique. However, low and erratic results were again obtained.

The method of Simonsen[12] for the dissolution of basic rocks was found to give reproducible results, with 80 per cent. recovery of the added platinum in the presence of sodium

silicate (Fig. 1, graph C). In this procedure the sample of sodium silicate containing added platinum was heated with 1 ml of concentrated nitric acid and 15 ml of 40 per cent. w/v hydrofluoric acid and evaporated to dryness in a PTFE beaker; 10 ml of aqua regia were added and the beaker covered before heating it for 2 hours, the cover being then removed and the solution evaporated to dryness. Ten millilitres of concentrated hydrochloric acid were added and the solution heated for 10 minutes. The normal procedure for the tin(II) chloride method was then followed. However, as this procedure is obviously too insensitive for the determination of the platinum levels required, the method was abandoned.

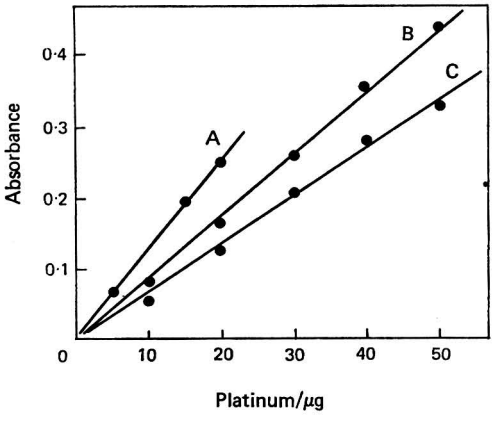

Fig. 1. Calibration graphs for the determination of platinum by the tin(II) chloride method after isopentyl acetate extraction of the tin(II) - platinum(II) chloride complex: A, 10 ml of isopentyl acetate; and B, 15 ml of isopentyl acetate; C, determination of platinum in the presence of 2 g of sodium silicate and extraction with 15 ml of isopentyl acetate

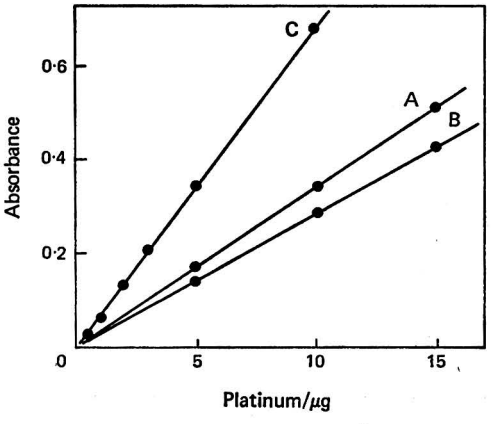

Fig. 2. Calibration graphs for the determination of platinum by the *p*-nitrosodimethylaniline method: A, standard platinum solutions made up to a final volume of 25 ml; B, standard platinum solutions in the presence and absence of sodium silicate, incorporating separation with tellurium, and with a final volume of 25 ml; and C, standard platinum solutions incorporating separation with tellurium, and with a final volume of 10 ml

p-*Nitrosodimethylaniline method*—The method of Kirkland and Yoe[9] was investigated by using pure platinum solutions and sodium silicate - platinum standards as before.

The pH of the required amount of standard platinum solution contained in a 25-ml calibrated flask was adjusted to between 2 and 3 with 0·1 M hydrochloric acid and the solution diluted to about 10 ml; 0·5 ml of buffer and 0·5 ml of reagent solutions were added and the flask washed down with a few millilitres of water. The solution was then heated in boiling water for 30 minutes to develop the colour of the platinum(II) - *p*-nitrosodimethylaniline complex. The solution was cooled in a bath of cold water, 5 ml of ethanol were added and the volume was made up to 25 ml with water. A blank solution was prepared in an identical way to correct for the excess of reagent in the sample solution. The absorbances of the solutions were measured at 525 nm against the blank, with 4-cm cells. The only difference between this procedure and the original method is that a final volume of 25 ml was used instead of 50 ml, with the corresponding alterations to the volumes of reactant solutions. The results, shown in Fig. 2 (graph A), indicate that it should be possible to determine 1 μg of platinum.

The method was then applied to sodium silicate containing known amounts of platinum, in the range 10 to 30 μg. The samples were brought into solution by heating them with 40 per cent. w/v hydrofluoric acid and evaporating to dryness, redissolving the residue in hydrochloric acid and adjusting the pH of the solutions to between 2 and 3 with sodium hydroxide solution before analysing them by the above procedure. No platinum was recovered. As the *p*-nitrosodimethylaniline method is known to be affected by several interferences a separation technique was introduced, based on the co-precipitation of platinum with tellurium. The method outlined by Sandell[20] was followed.

SEPARATION OF PLATINUM BY CO-PRECIPITATION WITH TELLURIUM—

About 50 ml of solution, 2·5 M in hydrochloric acid and containing 0·5 mg of tellurium(IV), as sodium tellurite, were treated at boiling temperature with 2 ml of a 25 per cent. solution of tin(II) chloride in 3 M hydrochloric acid. The precipitate was filtered on a sintered-glass crucible, washed with water and then dissolved in 2 ml of aqua regia and evaporated to dryness twice with hydrochloric acid in the presence of a few milligrams of potassium chloride. The residue was dissolved in 5 ml of concentrated hydrochloric acid and the pH brought to between 2 and 3 with sodium hydroxide or ammonia solution[9] before the determination of platinum was continued. Two problems were encountered in this procedure when it was applied to pure platinum solutions: (*i*) a white precipitate appeared during the reaction with *p*-nitrosodimethylaniline, which had to be removed by filtration before absorbance readings could be taken, and (*ii*) low and erratic results, with 40 to 60 per cent. recoveries, were observed.

The following parameters of the reaction were investigated to determine the causes of these discrepancies: the effect of nitric acid, which might remain after heating to dryness; the amount of potassium chloride used as the carrier; the effect of evaporating the samples to dryness or to small bulk; the effect of tellurium; and the effect of dissolving the potassium chloride residue in hydrochloric acid and adjusting the pH with sodium hydroxide solution.

From these experiments several conclusions were reached: recoveries were better by using the carrier and the amount of potassium chloride used was not critical; the precipitate occurring during the formation of the *p*-nitrosodimethylaniline - platinum complex is caused in some way by the presence of the tellurium. This precipitation could not be avoided but did not affect the recovery of platinum when removed by filtration; consistent results, with 85 per cent. recoveries, were obtained only when the final potassium chloride residue was dissolved by boiling with a few millilitres of water for 10 minutes followed by the addition of 1 drop of 4 M hydrochloric acid to bring the pH of the solution to between 2 and 3.

The reasons for the poor recoveries of platinum when the potassium chloride residue was dissolved in hydrochloric acid and neutralised with sodium hydroxide or ammonia solution are not clear as in the original method this appeared to be the correct procedure for neutralising strongly acidic solutions of platinum.[9] It is interesting to note that Russell, Spangenberg and Steele[2] experienced a similar problem in the determination of platinum by the tin(II) chloride method when the sample had been in contact with ammonia at any stage during the method.

A calibration graph was obtained for the determination of platinum incorporating the separation by co-precipitation with tellurium (Fig. 2, graph B), 85 per cent. recoveries being obtained with a coefficient of variation of 3 per cent.

This modified method was tested under simulated conditions for the analysis of glass by taking 1-g samples of sodium silicate to which additions of aliquots of a standard platinum solution had been made. The samples were evaporated to dryness with 5 ml of 40 per cent. w/v hydrofluoric acid in a PTFE beaker on a controlled-temperature hot-plate and the residues then dissolved by heating with 11 ml of concentrated hydrochloric acid before diluting to 50 ml of solution with water and again heating on a hot-plate for 15 minutes; 0·5 mg of tellurium was added to the filtered solution and the separation process continued as described previously. Recoveries were again found to be erratic and low, being in the range 5 to 30 per cent. Two variations on the previous procedure were examined to improve these recoveries. (*i*) The residue after evaporation to dryness with 40 per cent. w/v hydrofluoric acid was dissolved in water and the acidity then adjusted to 2·5 M with hydrochloric acid. With 10-μg additions of platinum to 1 g of sodium silicate 50 per cent. recoveries were obtained. (*ii*) The residue after evaporation to dryness with 40 per cent. w/v hydrofluoric acid was evaporated to dryness again with aqua regia. The residue was then dissolved in water as in (*i*). The results obtained by this method were identical with those obtained in the absence of sodium silicate (Fig. 2, graph B). An attempt was made to improve on the 85 per cent. recoveries obtained by making use of a double precipitation (two 0·5-mg and two 0·25-mg portions of tellurium) and different amounts of tellurium (0·25, 0·50 and 1·00 mg) but no improvement was observed.

The sensitivity of the method was finally improved by reducing the volume of solution used for absorbance measurements to 10 ml (Fig. 2, graph C). This enabled 0·4 μg of platinum,

in the presence of sodium silicate, to be determined, which gives a minimum determination level of 0·2 μg g^{-1} of platinum with a 2-g sample of glass.

Recommended procedure for the colorimetric determination of platinum in glass

Weigh 1 g of powdered glass into a PTFE beaker and add 10 ml of 40 per cent. w/v hydrofluoric acid. Evaporate the sample to dryness on a hot-plate thermostatically controlled at 220 °C, then evaporate to dryness again with 5 ml of aqua regia. Add 40 ml of water and heat nearly to boiling, then add 11 ml of concentrated hydrochloric acid and heat for a further 15 minutes. Add 0·25 mg of tellurium, as sodium tellurite, and 3 ml of 25 per cent. tin(II) chloride solution. Heat the solution and precipitate for 30 minutes, to facilitate coagulation, and then filter the mixture. Wash the precipitate with water and then dissolve it in 2 ml of aqua regia, returning this solution to the original PTFE beaker. Add about 15 mg of potassium chloride and by heating evaporate the solution to dryness, add 1 ml of hydrochloric acid and evaporate to dryness again. Dissolve the residue in 5 ml of water, by heating the mixture for 15 minutes on a hot-plate and then transfer the solution to a 10-ml calibrated flask. Cool the solution and adjust its pH to between 2 and 3 with 1 drop of 4 M hydrochloric acid, by using pH paper. Add 0·25 ml of buffer solution and 0·3 ml of *p*-nitrosodimethylaniline solution and immerse the flask in boiling water for 30 minutes. Immediately cool the flask in cold water and filter the solution, returning the filtrate to the calibrated flask, and make the volume up to 10 ml with water. Measure the absorbance of the solution at 525 nm in a 4-cm cell against a blank sample carried through the same procedure.

Prepare a standard calibration graph with known amounts of platinum by following the above method, omitting the glass sample.

Spark-source mass spectrography

Spark-source mass spectrography is now an established technique for trace-element analysis and has been applied to a wide variety of materials. It was considered therefore to be a potentially useful technique for the determination of platinum in glass.

Electrodes prepared by compressing powdered glass samples cannot be used directly because of the insulating properties of a silica matrix. If, however, electrodes are prepared[21] by mixing the glass with a conducting material, then it becomes possible to spark these electrodes in the normal way. Graphite and silver powders were both considered for mixing with the glass and proved to be of equal efficiency. Of the two, silver powder is slightly advantageous in that for an investigation of glass for other trace elements there are fewer possible interatomic species that can be formed which might interfere in the analysis. For this reason a silver - glass electrode system was chosen for a thorough investigation.

The sparking conditions found to be the most suitable are those shown in Table I. Under these conditions the time required to deposit a mass spectrum on the photographic plate in the range 0·001 to 200 nC was 2 to 3 hours. Increases in the frequency pulse length and spark voltage gave the expected increases in spark intensity but also caused overheating of the electrodes and the emission of electrode fragments, which contributed to a breakdown in the accelerating voltage in the source.

As the concentrations of the major constituents of the glass are usually known it was decided to use a minor isotope of one of these elements as the internal standard for the determination of platinum. For this purpose the calcium-42 isotope, at 0·64 per cent. natural abundance, was chosen as this would be present in the glass at a concentration of about 250 p.p.m. None of the isotopes of sodium or silicon could be used as their concentration levels in the glass would be too high.

Table I

Experimental sparking conditions for silver - glass electrodes

Spark:	voltage	20 kV
	pulse length	100 μs
	frequency	100 Hz
Beam chopper:	pulse length	5 μs
	frequency	Variable
Vacuum:	analyser	$<1 \times 10^{-7}$ torr
	source	$<1 \times 10^{-5}$ torr

Despite careful control of all sparking parameters it was impossible to reproduce results with glass samples containing known amounts of platinum. The measured sensitivity factors for platinum-194, 195 and 196 were found to vary by a factor of 2 or 3 between electrodes prepared from the same samples, although for any one electrode the values were in agreement with each other as regards their isotopic abundances. This would indicate two possible sources for the non-reproducibility: the calcium-42 standard line is not being reproduced satisfactorily; and the platinum is not present homogeneously in the samples.

As alkali and alkaline earth metals are susceptible to thermal ionisation from the electrodes it is possible that small variations in sparking conditions from one analysis to another could cause variations from the true calcium concentration in the ion beam. To overcome this possibility the silver powder was doped with 20 μg of niobium pentoxide per gram of silver powder and the niobium-93 line then used as the internal standard. The doped silver powder was sparked in the usual way to confirm that the niobiumpentoxide and the silver powder were thoroughly mixed. When this mixture was used to standardise the method for the determination of platinum in glass inconsistent values were again obtained for the sensitivity factors. This would indicate therefore that the platinum is not homogeneously mixed throughout the glass, which is not surprising considering the method of preparation. Because in a mass-spectrographic analysis only a few milligrams of the electrode are consumed, it is highly probable that in one analysis a non-representative result is obtained even although the powdered glass taken for the analysis is obtained from a much larger sample.

The poor reproducibility apart, the lowest level of platinum that could be quantitatively determined by using a maximum exposure of 200 nC was about 10 $\mu g\ g^{-1}$. This level of determination and reproducibility could be improved if the platinum was pre-concentrated by the tellurium co-precipitation method described above. It was felt, however, that this procedure would not be of practical use as the time needed for analysis of one sample by this method would be as long as that required for analysis by the chemical method described above. Further, while six glass samples can be analysed chemically in 1 day, 3 days would be required with the mass spectrograph. If, however, at some future date analyses of glasses for the determination of platinum at concentrations less than 0·1 $\mu g\ g^{-1}$ were required, then a pre-concentration method could be reconsidered.

X-RAY FLUORESCENCE SPECTROMETRY

Jenkins and De Vries[22] have indicated that by using a direct X-ray analytical method the limit of detection for platinum in a typical matrix would be about 20 $\mu g\ g^{-1}$. Examination of a glass sample containing 20 $\mu g\ g^{-1}$ of platinum, however, with the conditions outlined below, gave no measurable response, thereby confirming that a pre-concentration technique would be required to determine the low levels of platinum desired. The technique proposed by Luke[14] was adopted and co-precipitation with tellurium, as described above, was selected for concentrating the platinum, as this technique had proved to be successful in the *p*-nitroso-dimethylaniline colorimetric procedure.

After co-precipitation with tellurium, by the method described later, the platinum was filtered off on a Pyrex filter holder (supplied by the Millipore Corporation of Bedford, Mass., U.S.A.), as described by Luke,[14] with filter discs 25 mm in diameter with a 0·8-μm pore size. The filter discs were then removed from the filtration apparatus and fixed to a glass support disc with silicone grease. These were dried at 105 °C for 15 minutes and the intensity of the platinum Lα line was measured on the X-ray fluorescence spectrometer. The addition of boric acid to the solutions before co-precipitation of the platinum with tellurium was found to give 90 to 98 per cent. recoveries, while in the absence of boric acid only 59 to 95 per cent. recoveries were observed.

The following spectrometer conditions were used for measurements: lithium fluoride crystal, with the 200 plane with a 2*d* spacing of 0·402 8 nm, scintillation detector; and pulse height analyser with an analysis time of 300 s. The X-ray tube had a 1-kW tungsten anode, operating at 48 kV and 20 mA. A 0·05-mm nickel filter was used over the tube window to eliminate line overlap between platinum L and scattered tungsten L radiation. Samples were examined by using both a 160 and a 480-μm primary collimator. A 1-kW chromium-anode tube was also tried and found to give greater intensity accompanied, however, by a much greater background. Comparative results are tabulated in Table II.

TABLE II

COMPARISON OF TUNGSTEN-ANODE AND CHROMIUM-ANODE TUBES FOR THE DETERMINATION OF PLATINUM

Intensity measurements are in counts s^{-1}

Tube	Tungsten anode (nickel filter)				Chromium anode	
Collimator size	160 μm		480 μm		480 μm	
Platinum/μg	Intensity	Corrected intensity	Intensity	Corrected intensity	Intensity	Corrected intensity
0	53	—	187	—	610	—
10	103	50	293	106	772	162
20	148	95	377	190	926	316
30	193	140	497	310	1 072	462
40	233	180	570	383	1 246	636
50	283	230	683	496	1 451	841

Jenkins and De Vries[22] have shown that the percentage error in a determination is given by the product—

$$\frac{100}{\sqrt{T}} \cdot \frac{1}{\sqrt{R_p} - \sqrt{R_b}}$$

where T is the counting time, R_p the count-rate of peak and R_b the count-rate of background.

From the results given in Table II, the calculated values of this product show that the tungsten anode with a 480-μm collimator provides the most accurate results.

The fractional 2σ counting error for a 10-μg platinum standard and an analysis time of 300 s was calculated to correspond to $\pm 0{\cdot}24$ μg.

The co-precipitation X-ray technique was found, in practice, to give a relative standard deviation of 10 per cent., with a lower determination limit of 0·5 μg. Some typical results are given in Table III. The total time required for the analysis is between 3 and 4 hours.

TABLE III

CALIBRATION FOR THE X-RAY FLUORESCENCE DETERMINATION OF 0 TO 10 μg OF PLATINUM IN GLASS BY USING THE CONDITIONS DESCRIBED

Platinum/μg	Intensity/ counts s^{-1}	Corrected intensity/ counts s^{-1}
0	180	—
2	206	26
4	224	44
6	235	55
8	260	80
10	286	106

RECOMMENDED PROCEDURE FOR THE X-RAY FLUORESCENCE DETERMINATION OF PLATINUM IN GLASS—

Weigh 1 g of powdered glass into a PTFE beaker and add 10 ml of 40 per cent. hydrofluoric acid. Evaporate the sample to low bulk on a hot-plate thermostatically controlled at 220 °C. Add 11 ml of concentrated hydrochloric acid and boil the solution for 20 minutes. Cool and dilute the solution to about 50 ml, add 5 ml of 5 per cent. boric acid solution and boil for 5 minutes. Add 0·25 mg of tellurium, as sodium tellurite, and 5 ml of 25 per cent. tin(II) chloride solution. Collect the precipitate on a 25-mm Millipore filter and wash it with 2 to 3 ml of water. Fasten the filter disc to a glass support with silicone grease and dry at 105 °C for 15 minutes. Finally, measure the intensity of the platinum Lα radiation by using an X-ray fluorescence spectrometer. Use a 480-μm primary collimator and a tungsten-anode tube, fitted with a nickel filter, as the X-ray source.

Calibration graphs are constructed by taking standard platinum solutions through the same procedure, omitting the powdered glass. This simpler X-ray fluorescence method of analysis has been adopted in our laboratories for the routine determination of platinum in several different types of glass. The modified dissolution technique used here has not been examined for use in the colorimetric procedure.

ANALYSIS OF GLASS SAMPLES—

The standard glasses were prepared by dissolving known amounts of platinum in aqua regia and adding these to the sodium silicate batch. The batches were dried and mixed and then used to prepare the glasses. The initial melting of the glass was carried out in an alumina crucible but it was necessary to homogenise the glasses for 2 hours in a platinum crucible. Results for the analysis of these standards by the *p*-nitrosodimethylaniline colorimetric method and the X-ray fluorescence technique are shown in Table IV. The results confirm that platinum is leached from the crucibles in the homogenising stage and also that homogenisation of the platinum within the glass does not take place completely.

TABLE IV

ANALYSIS OF PLATINUM STANDARDS BY THE *p*-NITROSODIMETHYLANILINE COLORIMETRIC AND X-RAY FLUORESCENCE TECHNIQUES

Concentration of platinum added to glass/μg g^{-1}	Concentration of platinum found/μg g^{-1}	
	X-ray fluorescence	Colorimetric
0	3·1	5·5
5	7·9	8·0
10	17·2	14·0
20	23·8	23·0
30	29·0	30·5

TABLE V

DETERMINATION OF PLATINUM IN GLASS SAMPLES BY THE *p*-NITROSODIMETHYLANILINE AND X-RAY FLUORESENCE METHODS

Glass type	Platinum/μg g^{-1}, by—	
	Colorimetry	X-ray fluorescence
Sodium - calcium - silica A	19	22
B	19	17
C	6·4	6·0
D	0·4	0·6
Lead - sodium - silica E	2·3	3·0
F	0·5	0·7

Analysis of sodium - calcium silicate glasses and lead oxide - silica glasses have been made by using these procedures and some typical results are given in Table V. The colorimetric and X-ray fluorescence methods give results that are generally in good agreement.

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Rapid Methods for the Determination of Low Concentrations of Total Sulphur in Liquids and Gases

Part I. The Determination of Total Sulphur in Light Petroleum Distillate by Reduction with Raney Nickel*

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Granatelli's method for the determination of sulphur in liquid hydrocarbons has been modified to permit the determination of total sulphur in purified light petroleum distillate at concentrations below 4·0 p.p.m. w/v. A mixture of propan-2-ol and water is used as the reaction solvent in a rapid method for the determination of total sulphur in light petroleum distillate in the range 0·1 to 4·0 p.p.m. w/v with a precision of ±9 per cent. of the determined value. For concentrations in the range 0·01 to 0·10 p.p.m. a more lengthy method is given, which has an absolute precision of ±0·01 p.p.m. w/v.

THE manufacture of synthesis gas for the production of ammonia and methanol is now largely based on feedstocks of light petroleum naphtha or natural gas. Both feedstocks contain compounds of sulphur that must be removed before they are brought into contact with the nickel-containing reformer catalysts. Light petroleum naphtha usually contains between 40 and 1 000 p.p.m. of total sulphur but desulphurised naphtha contains only 1 p.p.m. or less. Total sulphur can be determined in crude liquid feedstocks by a method published by the Institute of Petroleum[1] and another by the International Conference of Benzole Producers.[2] These two methods are based on that of Wickbold[3] and all three methods involve the complete oxidation of the sample with air or oxygen. Complete oxidation is time consuming and reproducibility is poor with low concentrations of sulphur. Much time can be saved by using when possible the reduction method recommended by Granatelli,[4] in which the sample is treated first with a suspension of Raney nickel in propan-2-ol to fix the combined sulphur as nickel sulphide and then with hydrochloric acid to liberate the sulphur as hydrogen sulphide, which is then absorbed in alkali and titrated. The method tends to give erratic results with low concentrations of sulphur, but in the modification described below satisfactory results are obtained by using a mixture of propan-2-ol and water instead of pure propan-2-ol as a solvent in the reaction with Raney nickel (Method 1).

While the modified procedure gave satisfactory results with concentrations of sulphur in excess of 0·1 p.p.m. its precision was poor at concentrations below that level. Three possible reasons were the imprecise visual end-point, variation of the reagent blank, and the inhibiting effect of the organic phase on the release of hydrogen sulphide from the acidified reaction mixture. The organic phase used could reduce the temperature of the boiling reaction mixture and dissolve trace amounts of the hydrogen sulphide evolved. With the elimination of these sources of error a method was produced that could be used for concentrations of sulphur below 0·1 p.p.m. To make use of a more dilute titrant the final titration with the visual end-point was replaced by a spectrophotometric method based on one used by Rees and Hill[5] for the determination of trace amounts of sulphate in water. Preparation of active Raney nickel *in situ* was introduced to eliminate variation in the reagent blank, while interference from the organic phase was prevented by separating the sulphided Raney nickel from the organic liquids by filtration and then boiling it with hydrochloric acid alone to liberate hydrogen sulphide.

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METHOD 1. TITRIMETRIC DETERMINATION OF TOTAL SULPHUR IN LIGHT PETROLEUM NAPHTHA CONTAINING BETWEEN 0·1 AND 4·0 P.P.M. OF SULPHUR

APPARATUS—

A combined reflux and regeneration apparatus, as shown in Fig. 1, was used.

REAGENTS—

Sodium hydroxide solution, 4 per cent. w/v, aqueous.

Propan-2-ol - water mixture—Add 5 ml of distilled water to 95 ml of analytical-reagent grade propan-2-ol.

Hydrochloric acid, 40 per cent. v/v.

Dithizone indicator—Dissolve 10 mg of analytical-reagent grade dithizone in 50 ml of analytical-reagent grade acetone. This solution should be made up daily and stored in the dark.

Stock standard solution of mercury(II) acetate—Dry mercury(II) acetate in an oven at 150 °C (assay not less than 99·0 per cent. on the dried material). Dissolve 3·38 g of the dried reagent in a mixture of 16·5 ml of glacial acetic acid and 25 ml of water. Make the volume up to 500 ml with water.

(1 ml of solution ≡ 1 000 μg of sulphur.)

Dilute standard solution of mercury(II) acetate—Dilute 10 ml of the stock solution to 100 ml with water. Dilute 25 ml of this solution to 100 ml with water.

(1 ml of solution ≡ 25 μg of sulphur.)

Suspension of Raney nickel—Dissolve 10 g of analytical-reagent grade sodium hydroxide pellets in 100 ml of water. Cool the solution in an ice-bath, then add slowly 10 g of nickel - aluminium alloy (B.D.H.) and allow the mixture to stand for half an hour. Decant the aqueous layer, wash three times with 100 ml of water by decantation and add 100 ml of propan-2-ol; preserve in a stoppered flask. It must not be used if more than 3 days old.

Nitrogen or argon—Use a supply that is essentially free of oxygen and sulphur.

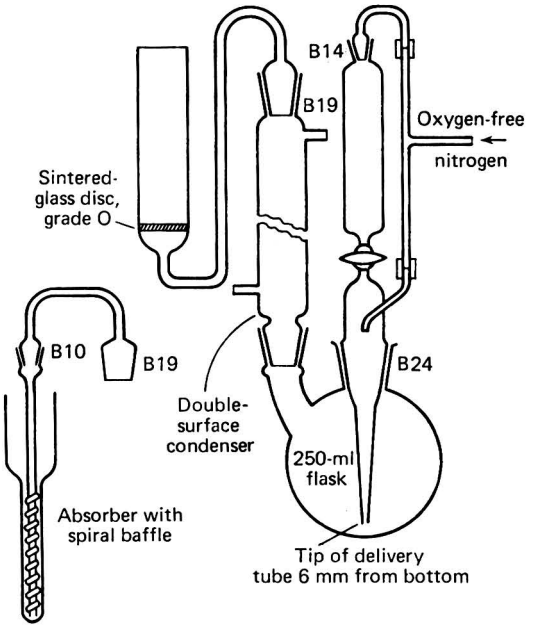

Fig. 1. Apparatus for the determination of sulphur in light distillate by reduction with Raney nickel

PROCEDURE—

Assemble the apparatus shown in Fig. 1. Measure 20 ml of 4 per cent. sodium hydroxide solution into the absorber with the sintered disc and 50 ml of the dilute hydrochloric acid solution into the tap funnel, then close all the joints and sweep out the apparatus with nitrogen. Raise the tap funnel and measure into the flask, by a pipette with a large delivery jet, 10 ml of a well stirred suspension of Raney nickel. Add 20 ml of propan-2-ol - water mixture followed by 50 to 70 ml of the sample, replace the tap funnel and reduce the flow of nitrogen to 2 bubbles per second (2 to 3 l hour^{-1}). Heat the mixture to boiling under reflux for half an hour, then cool it to below the boiling-point and run in the hydrochloric acid from the tap funnel, dropwise, over a period of 10 minutes. Increase the flow of nitrogen to about three times its former rate and boil until all of the Raney nickel has dissolved. Add to the sodium hydroxide solution in the absorber 2 or 3 drops of indicator and 20 ml of analytical-reagent grade acetone. Titrate the absorbed sulphide with the standard solution of mercury(II) acetate by using a 5-ml microburette, making sure that all of the liquid above and below the sintered disc is titrated (Note 1). Carry out a blank test exactly as above omitting only the sample (Note 2). If A ml is the volume of titrant used for the test, B ml is the volume of titrant used for the blank and V ml is the volume of sample taken, then

$$\text{Total sulphur (S)} = \frac{(A - B) \times 25}{V} \text{ p.p.m. w/v}$$

NOTES—

1. The absorption of hydrogen sulphide takes place substantially on the underside of the sintered disc. It is therefore essential that the disc is repeatedly washed with the titrated solution to ensure complete titration of the sodium sulphide.

2. A blank test must be performed on every batch of suspension and when a new supply of propan-2-ol is used.

EXPERIMENTAL

Granatelli's method has been used successfully for hydrocarbon distillates containing between 100 and 600 p.p.m. of total sulphur. For the analysis of purified petroleum distillates containing about 1·0 p.p.m. of sulphur the method gave erratic results. Increasing the amount of sample taken to improve the sensitivity only resulted in a lower recovery of sulphur. Good recoveries were obtained over a wide range of concentrations when a definite amount of water equivalent to 5 per cent. v/v of the added propan-2-ol was present during the reduction. Factitious samples were prepared by adding, from a 1-ml microburette, measured volumes of a crude light petroleum distillate to measured amounts of a light distillate that had been desulphurised completely by refluxing with an excess of Raney nickel.

TABLE I

DETERMINATION OF TOTAL SULPHUR IN LIGHT PETROLEUM DISTILLATE

Desulphurised (light distillate/ml	Distilled water added/ml	Propan-2-ol added/ml	Raney nickel suspension/ml	Standard added, crude light distillate/ml	Titre/ml	Sulphur added/μg	Sulphur recovered/μg	Recovery, per cent.
70	1	19	10	Nil	0·34	Nil	—	Blank
70	1	19	10	0·1	0·96	14·2	15·5	109
70	1	19	10	0·5	3·24	71·0	72·5	102
70	1	19	10	1·0	5·94	142·0	140·0	99
70	1	19	10	1·5	8·72	213·0	209·0	98
100	2	38	20	0·2	1·74	28·4	27·5	97
100	2	38	20	0·4	3·06	56·8	60·5	106
100	2	38	20	0·4	3·06	56·8	60·5	106
100	2	38	20	0·6	4·34	85·2	92·5	108
100	2	38	20	1·0	6·20	142·0	140·0	99
100	2	38	20	Nil	0·64	Nil	—	Blank
100	2	38	20	Nil	0·60	Nil	—	Blank
Nil	2	38	20	Nil	0·66	Nil	—	Blank

The crude distillate had been analysed by Method 1 (142 p.p.m. w/v as sulphur) and by an oxidation method[2] (144 p.p.m. w/v as sulphur). The mixtures were then analysed by the Raney nickel reduction procedure as in Method 1, taking the whole treated volume of 70 ml for each analysis. A further series of factitious samples was prepared by treating 100-ml portions of the desulphurised light petroleum distillate with measured volumes of the analysed crude distillate, but these samples were treated with twice the normal amount of the suspension of Raney nickel during the subsequent analysis. Finally, blank tests were carried out on the desulphurised light distillate, the propan-2-ol and the suspension of Raney nickel.

The results in Table I show that over a wide range of concentrations the recovery of sulphur by Method 1 is satisfactory and that there is no great disadvantage in taking rather more of the sample if additional Raney nickel is used.

The light distillate chosen as a standard for these experiments contained substantial amounts of only two types of sulphur compound (Table II, column A). Although this light distillate was fairly typical it was thought desirable to test by the recommended method some material that had a different composition. Two additional samples (Table II, columns B and C) were analysed by oxidation Method 2 and by Method 1. Methods derived from those of Ball[6] were used to determine the concentrations of the types of combined sulphur and the concentration of the elemental sulphur.

TABLE II

TYPES OF SULPHUR COMPOUND IN THREE SAMPLES OF LIGHT PETROLEUM DISTILLATE (P.P.M. W/V)

	Sample A	Sample B	Sample C
H_2S	<2	<2	<2
RSH	73	84	61
R_2S_2	5	14	11
R_2S	59	71	72
Elemental	1	7	24
Non-reactive	1	20	22
Total sulphur by oxidation method ..	144	191	188 191 193
Total sulphur by reduction method ..	142	190 190	188 190 192

The three samples of analysed light distillate were then used to prepare samples containing low concentrations of sulphur, by adding small amounts to measured volumes of desulphurised light distillate. The analyses of these factitious samples by Method 1 are compared in Table III where it can be seen that the recovery of sulphur at low levels of concentration is satisfactory. The repeatability of the method is largely dependent on the constancy of the blank for a particular batch of reagents. The coefficient of variation of the nine results shown in Table I is 4·3 per cent., corresponding to a range of $\pm 0{\cdot}09$ p.p.m. at the 1·0 p.p.m. level, but this variation includes errors associated with the preparation of the factitious standards; the analytical error would be less.

TABLE III

DETERMINATION OF TOTAL SULPHUR IN THREE SAMPLES OF LIGHT PETROLEUM DISTILLATE

Sample (see Table II)	Sulphur in 50 ml of distillate/μg		Sulphur, p.p.m. w/v	
	Introduced	Found	Introduced	Found
A	14·2	14·5	0·28	0·29
	71·0	69·9	1·42	1·39
B	76·0	81·0	1·52	1·62
C	19·0	17·5	0·38	0·35
	76·0	71·0	1·52	1·42

METHOD 2. TITRIMETRIC DETERMINATION OF TOTAL SULPHUR IN LIGHT PETROLEUM DISTILLATE CONTAINING BETWEEN 0·01 AND 0·10 P.P.M. W/V

APPARATUS—

A combined reflux and regeneration apparatus, as shown in Fig. 1, fitted with the absorber with the spiral baffle, and a Unicam SP600 spectrophotometer or equivalent instrument with special absorption cell fitted with stirrer and burette, as shown in Fig. 2, were used.

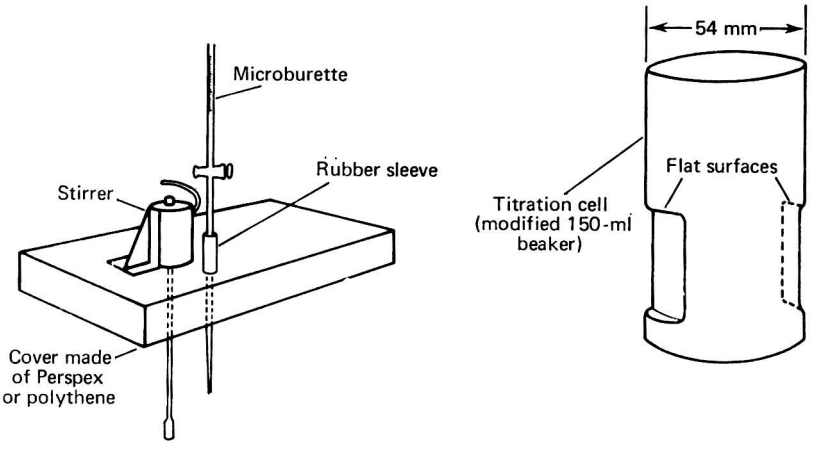

Fig. 2. Titration cell, cover and stirrer for spectrophotometric finish with the Unicam SP600 spectrophotometer

REAGENTS—

As in Method 1 except for those listed below. All aqueous solutions must be prepared with boiled-out water.

Sodium hydroxide solution, 10 per cent. w/v, aqueous.

Propan-2-ol - water mixture—Add 3·5 ml of water to 96·5 ml of analytical-reagent grade propan-2-ol.

Stock standard solution of mercury(II) acetate—As in Method 1.

Working standard solution of mercury(II) acetate—Make the solution up for use as in Method 1 and dilute 20 ml of this final solution to 250 ml with water.

(1 ml of solution ≡ 2 μg of sulphur.)

PROCEDURE—

Activation in situ of the Raney nickel—Measure 10 ml of 10 per cent. sodium hydroxide solution into the digestion flask of the modified reflux apparatus (Fig. 1). Heat it to about 90 °C, allow it to cool and add 1·000 g of nickel - aluminium alloy. Allow the reaction to proceed for 10 to 15 minutes and add 10 ml of distilled water. Decant the aqueous layer and wash the nickel twice with 10 ml of water, once with a mixture of 10 ml of water and 10 ml of propan-2-ol and again with 10 ml of pure propan-2-ol.

Treatment of sample—Add 50 ml of the sample of light distillate and 30 ml of the propan-2-ol - water mixture to the flask and place 4·0 ml of 4 per cent. w/v sodium hydroxide solution in the absorber with the spiral baffle. Reduce the sample under reflux for half an hour in an atmosphere of nitrogen, cool, then decant the contents of the reaction flask through a No. 40 Whatman filter-paper. Wash the sulphided nickel on the filter with 20 ml of propan-2-ol before folding the filter-paper and placing it with the sulphided Raney nickel back into the reaction flask, taking care to remove any nickel adhering to the ground-glass joint. Re-assemble the apparatus with 50 ml of 40 per cent. v/v hydrochloric acid in the funnel, purge with nitrogen and slowly add the hydrochloric acid. Bring the contents of the flask

to boiling and boil for half an hour. Disconnect the absorber and transfer its contents quantitatively to the spectrophotometric cell (Fig. 2) with a minimum amount of boiled-out distilled water. Make this volume up to 50 ml with boiled-out water and then add 25 ml of analytical-reagent grade acetone and 0·50 ml of dithizone solution.

Spectrophotometric titration—Place the cell and its contents in a Unicam SP600 spectrophotometer and assemble the stirrer motor and burette unit (Fig. 2). Set the wavelength control to 550 nm, the transmission - density scale to zero and adjust the needle to zero with the dark-current control. Start the stirrer, switch to the "Test" position and re-adjust the needle to zero with the slit width control. Several minutes may elapse before the solution is thoroughly mixed and equilibrium is reached. Add the standard mercury(II) acetate working solution from a 5-ml microburette in 0·20-ml increments, pausing between each addition to note any deflection of the needle. When the first deflection occurs note the volume of mercury(II) acetate added and measure the optical density on the transmission - density scale by adjusting the needle back to zero. Continue adding mercury(II) acetate in 0·20-ml increments, noting the volume added and the optical density in each instance, until a further four readings have been made.

Draw a graph relating millilitres of titrant to optical density and determine the end-point to the nearest 0·05 ml from the point of intersection between the rising and horizontal parts of the graph.

A blank determination must be carried out exactly as above omitting only the sample.

CALCULATION—

Let T_S be the number of millilitres of mercury(II) acetate used for sample titration

and T_B be the number of millilitres of mercury(II) acetate used for blank titration,

then $$\frac{2\,(T_S - T_B)}{50} = \text{concentration of sulphur in parts per million w/v.}$$

EXPERIMENTAL

To test the procedure on samples of known sulphur content it was necessary first to prepare sulphur-free light distillate by the repeated distillation of a purified distillate with Raney nickel until no sulphur could be detected in the product by Method 2. The precise sulphur content of a prepared light distillate containing about 5 p.p.m. of sulphur was then

TABLE IV

SULPHUR DETERMINATIONS ON 50-ml SAMPLES OF LIGHT DISTILLATE

Sample	(A) Sulphur added		(B) Sulphur recovered		(B)–(A),	Difference between duplicates,
	μg	p.p.m. w/v	μg	p.p.m. w/v	p.p.m. w/v	p.p.m. w/v
Reagent blanks (no light distillate)	—	—	3·80	0·076	—	0·002
	—	—	3·90	0·076	—	
Reagents *plus* sulphur-free light distillate	Nil	Nil	3·50	0·070	—	0·006
	Nil	Nil	3·80	0·076	—	
Factitious samples						
1	1·13	0·023	0·85	0·017	−0·006	0·010
	1·13	0·023	1·35	0·027	+0·004	
2	2·25	0·045	2·65	0·053	+0·008	0·004
	2·25	0·045	2·45	0·049	+0·004	
3	3·38	0·068	3·25	0·065	−0·003	0·006
	3·38	0·068	3·55	0·071	+0·003	
	3·38	0·068	3·35	0·067	−0·001	0·006
	3·38	0·068	3·05	0·061	−0·007	
4	4·50	0·090	5·05	0·101	+0·011	0·006
	4·50	0·090	4·75	0·095	+0·005	
5	5·62	0·112	6·15	0·123	+0·011	0·004
	5·62	0·112	6·35	0·127	+0·015	

determined by the same method, except for the final titration for which the procedure detailed in Method 1 was used (*i.e.*, a more concentrated titrant and a visual end-point). This prepared distillate was used as a standard solution (1 ml of solution ≡ 5·62 μg of sulphur) in all subsequent work.

To several individual samples of sulphur-free light distillate, each of 50-ml volume, varying amounts of the standard light distillate were added, *viz.*, 0·20, 0·40, 0·60, 0·80 and 1·00 ml, and these samples were analysed in duplicate for sulphur content by Method 2. The results obtained are given in Table IV, where it can be seen that although the differences between added and recovered sulphur ranged from −0·007 to +0·015 p.p.m., the differences between duplicates varied only from 0·002 to 0·010 p.p.m. Thus it is possible to determine total sulphur by this method at concentrations down to 0·01 p.p.m. w/v with a precision of ±0·01 p.p.m. w/v, although strict attention to detail is essential as the amounts of sulphur to be determined may be less than the amount of sulphur present in the reagents.

Discussion

Several modifications to Granatelli's original method have been proposed. Reed[7] activated the nickel - aluminium alloy *in situ* with boiling sodium hydroxide solution and Pitt and Rupprecht[8] used a colorimetric finish in which the liberated hydrogen sulphide was converted into methylene blue by reaction with an iron(III) salt and *NN*-dimethyl-*p*-phenylenediamine, which was then measured spectrophotometrically. This latter procedure is more sensitive than the titrimetric finish described in Method 1 but the determination takes more time. The titrimetric method has the added advantage of being more readily applicable to samples of widely varying composition. The analysis of a sample with a sulphur content above the prescribed limits can usually be completed by using additional titrant or a more concentrated titrant. Attempts to use a lead sulphide stain finish, as described in a British Standard method for hydrogen sulphide in fuel gas,[9] were unsuccessful because the range of stains that could be measured accurately was too narrow (1 to 10 μg of sulphur) and the reagent blank was too large. Virtually all of the reagent blank originated from the Raney nickel but some batches of propan-2-ol contained sulphur. Thus in Method 1 it was only necessary to determine a blank on each preparation of active suspension and on each batch of propan-2-ol. Sulphur was easily removed from impure propan-2-ol by refluxing it with an excess of Raney nickel.

The method has been used successfully for the determination of total sulphur in crude distillates, kerosine and hydrorefined distillates, but not for sulphur in gas oils. According to Granatelli[4] olefines interfere in the reaction and compounds such as sulphoxides or sulphones are reduced with difficulty or not at all. In most instances the interference from olefines is negligible if they are present at concentrations less than 2 per cent., but if oxygenated compounds are present one of the oxidation procedures already cited should be used. Alternatively, the microcoulometric system used by Martin and Grant,[10] in which the sample is first pyrolysed in oxygen, can be used. The Dohrmann microcoulometer C–200A can be used to determine sulphur in naphthas, kerosine and gas oils with a precision of ±1·0 p.p.m. if the concentration of sulphur is above 5 p.p.m. A full description has recently been published by Killer and Underhill.[11]

Method 2 has been used only to determine total sulphur in a few highly refined feedstocks used for experimental work. To obtain satisfactory results it is essential that the experimental conditions are strictly adhered to, and on no account should the volume of the sample exceed 50 ml. Tests should be carried out in duplicate and in an atmosphere free from volatile compounds of sulphur. Finally it must be emphasised that the method as given applies only to light petroleum distillate, which normally contains no oxygenated compounds of sulphur. Its applicability to other samples must be checked by methods similar to those outlined above before its use can be extended as the efficacy of the Raney nickel reduction procedure cannot be predicted with certainty.

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Rapid Methods for the Determination of Low Concentrations of Total Sulphur in Liquids and Gases

Part II. The Determination of Total Sulphur in Natural Gas and Synthesis Gases*

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A rapid method developed for the determination of total sulphur in light petroleum distillate is applied to the determination of total sulphur in natural gas. The sulphur compounds present in the gas are adsorbed on to a small amount of active carbon, which is then allowed to react with a suspension of Raney nickel in a water - propan-2-ol mixture and the sulphur determined as sulphide as described in Part I of this paper. An alternative procedure for the determination of total sulphur in gases containing compounds that are not reduced by Raney nickel is also described. The compounds of sulphur are adsorbed on to active carbon, desorbed into a stream of hydrogen, which then passes through a furnace at 900 °C, and the resulting hydrogen sulphide is determined as a stain on paper impregnated with lead acetate. Methods involving the use of a carbon adsorption tube give results with a precision of $\pm 0{\cdot}5$ mg m^{-3} of sulphur on samples of stenched natural gas.

MUCH of the natural gas from the North Sea is almost odourless as it is substantially free from compounds of sulphur.[1] A few parts per million of sulphur-containing compounds with strong smells are therefore added so that leaks in the distribution system can be easily detected. Tetrahydrothiophen was formerly used as a stenching agent for North Sea gas but this was replaced by a mixture of 90 per cent. of crude dimethyl sulphide and 10 per cent. of mixed thiols known as Calodorant F. Manufactured gases used for the synthesis of ammonia and methanol may contain similar compounds as well as carbonyl sulphide that has been formed by reaction with the carbon monoxide present. The total combined sulphur present in crude or doped gases is not normally more than a few parts per million, expressed as sulphur, and only 0·1 p.p.m. or less in purified gases. Concentrations of sulphur in the part per million range are determined by oxidation methods adapted from those for determining sulphur in liquids but the procedures are inconvenient and slow. Reduction methods are invariably more sensitive and faster than oxidation methods because the conversion of the whole sample is not necessary and the final tests for hydrogen sulphide are much more sensitive than those readily available for sulphate. In the methods to be described advantage has been taken of the adsorptive properties of active carbon for the application of reduction methods to the determination of total sulphur in gases. Non-oxygenated compounds of sulphur are adsorbed on to active carbon and determined by the Raney nickel reduction method developed for the analysis of petroleum distillates, but oxygenated compounds of sulphur must be desorbed from the active carbon and reduced to hydrogen sulphide by reaction with hydrogen at a high temperature.

METHOD A. RAPID DETERMINATION OF VOLATILE SULPHUR COMPOUNDS IN NATURAL GAS (REDUCTION WITH RANEY NICKEL)

APPARATUS—

Adsorption tube—Pack 1 g of prepared active carbon into a Pyrex glass tube, 130 × 5 mm i.d., keeping it in place with small plugs of glass-wool. Connect the tube with a short piece

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of silicone rubber tubing to a source of sulphur-free nitrogen and pass the gas through the carbon at the rate of about 30 l hour^{-1} while heating the outside of the tube to redness. Continue to pass nitrogen through the tube as it is allowed to cool, then seal it at both ends with silicone rubber stoppers.

Hamilton gas syringe, 1 litre.

Apparatus for reduction with Raney nickel—As in Method 1, Part I (this issue, p. 186).

REAGENTS—

Prepared active carbon—Reflux 50 g of activated carbon (Sutcliffe Speakman Quality 207, Type C, 14 to 18 mesh) with 100 ml of 20 per cent. v/v hydrochloric acid for 1·5 hours. Cool, filter the mixture on a Buchner filter and wash well with de-ionised water. Wash once with propan-2-ol and twice more with de-ionised water. Dry in an oven at 105 °C for 1 hour in a clean sulphur-free atmosphere.

Reagents for the reduction procedure with Raney nickel—As in Method 1, Part I.

PROCEDURE—

With a 1-litre gas syringe pass 2 litres of sample, measured at atmospheric pressure, through a prepared adsorption tube and seal both ends with silicone rubber stoppers. Assemble the apparatus as shown in Fig. 1, Part I.

Measure 20 ml of 4 per cent. sodium hydroxide solution into the cylindrical absorber and 50 ml of dilute hydrochloric acid into the tap funnel. Sweep out the apparatus with a stream of sulphur-free nitrogen. Raise the tap funnel and measure into the flask, by a pipette with an enlarged jet, 10 ml of well stirred Raney nickel suspension, then add 20 ml of propan-2-ol - water mixture. Finally empty the contents of the activated carbon adsorption tube, including the glass-wool plugs, into the flask. Replace the tap funnel and continue the determination of the sulphur in the charcoal as described under Method 1, Part I, for the determination of sulphur in petroleum naphtha. Finally determine the blank on the contents of an adsorption tube prepared from the same active carbon in the same way and with the same reagents. This blank test should be equivalent to less than 2 μg of sulphur.

If A ml is the volume of titrant used for the test, B ml is the volume used for the blank and V is the volume of gas taken in litres, then

$$\text{Total sulphur (S)} = \frac{(A - B) \times 25}{V} \text{ mg m}^{-3}$$

or

$$\frac{(A - B) \times 18{\cdot}7}{V} \text{ p.p.m. v/v at 20 °C.}$$

EXPERIMENTAL

The procedure was tested on gases doped with dimethyl sulphide, thiophen, tetrahydrothiophen and sulphur dioxide.

Standard solutions of dimethyl sulphide (B.D.H. laboratory reagent) were prepared freshly each day by dissolving weighed amounts of the pure liquid in known volumes of sulphur-free light petroleum distillate. The purity of the dimethyl sulphide used was checked by analysing a standard solution that had been made up gravimetrically and was deemed to contain 1·7 g of dimethyl sulphide per 100 ml, expressed as sulphur. Analysis based on total combustion of the sample[2] gave a total sulphur content of 1·67 g per 100 ml. As the difference was within the expected precision of the method it was assumed that the dimethyl sulphide was substantially pure and that the standards made up gravimetrically were correct.

Several tubes containing activated carbon were prepared as described in Method A. Each tube was then connected to a supply of sulphur-free nitrogen and 30 litres of nitrogen were passed through each tube at a rate of 50 l hour^{-1} while a calculated amount of standard solution was injected by microsyringe through a rubber septum into the nitrogen up-stream from the carbon. The carbon in each tube was then analysed as described in Method 1, Part I. The results given in Table I have been corrected for the amount of sulphur found in portions of active carbon that had not been exposed to a gas containing compounds of sulphur.

TABLE I

RECOVERY OF DIMETHYL SULPHIDE FROM A GAS

Dimethyl sulphide (expressed as sulphur) added to 30 litres of nitrogen/μg ..	25	50	100	150	184	200	368	552	736	920	Nil (blank)
Dimethyl sulphide (expressed as sulphur) found/μg	27	48	96	145	175	197	335	535	735	900	2

Further experiments showed that dimethyl sulphide in dry methane or methane saturated with water vapour at 20 °C and at concentrations between 0·4 and 4·0 p.p.m. v/v could be determined with a precision of ±7 per cent. of the determined value. Similar studies on the recovery of thiophen and tetrahydrothiophen were carried out in which solutions of the sulphur compounds in methanol were injected into known volumes of nitrogen. From gases containing between 0·8 and 1·6 p.p.m. of thiophen and tetrahydrothiophen the recovery of total sulphur was virtually complete when the volume of sample was not more than 50 litres. Tetrahydrothiophen is resistant to reduction by Raney nickel but amounts of 100 μg or less can be reduced quantitatively by the procedure used in these tests. The amount of sulphur that could be recovered by this technique from a gas containing volatile sulphur only as sulphur dioxide was negligible. The procedure could therefore be used to determine organic and inorganic sulphides in the atmosphere without interference from the usual excess of sulphur dioxide.

METHOD B. DETERMINATION OF VOLATILE COMPOUNDS OF SULPHUR IN SYNTHESIS GAS (REDUCTION WITH HYDROGEN AT HIGH TEMPERATURE)

APPARATUS (see Fig. 1)—

Adsorption tube—Pack 1 g of active carbon, which has been acid washed as described under method A, into a piece of silica tubing, 220 × 6 mm i.d., and keep it in place with plugs of silica-wool. Activate the tube as described under "Procedure" below.

Sleeve furnace to take adsorption tube—This was 150 mm long, wound to give a temperature of 900 °C and fitted with a rheostat control.

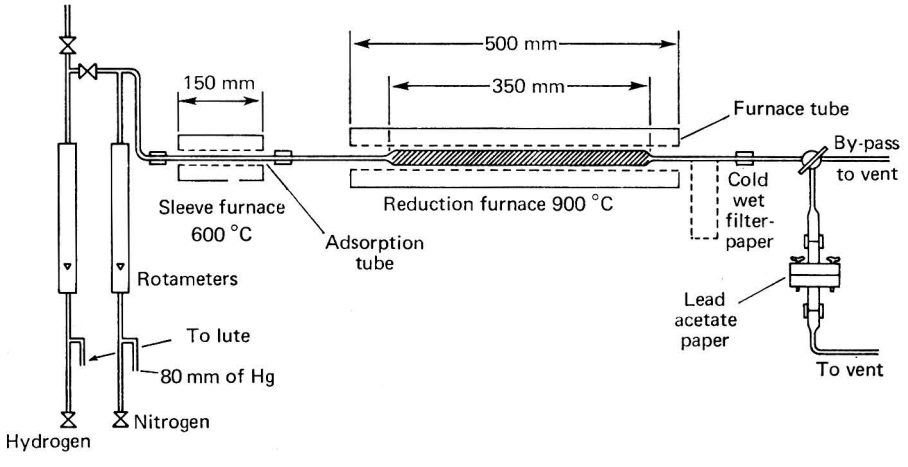

Fig. 1. Apparatus for the determination of total sulphur in synthesis gas

Furnace tube—This consisted of a packed length of silica tubing, 350 × 15 mm i.d., filled with acid-washed silica chips of 3 to 6 mm diameter. Inlet and exit connections were of 6 mm i.d.

Reduction furnace to take furnace tube—This was 500 mm long, wound to give a temperature of 900 °C and fitted with a rheostat control.

Holder for lead acetate papers—To enable the exposed part of the paper to be a circle of diameter 12·5 ± 0·25 mm.

Lead acetate papers—Prepare an aqueous solution containing 25 g of analytical-reagent grade lead acetate, 12·5 ml of glacial acetic acid and 40 ml of B.P. quality glycerol. Dilute the solution to 250 ml with water. Cut strips 38 mm wide from a sheet of Postlip 633 extra thick white paper (18 × 24, 6076) and soak them in the solution of lead acetate. Suspend the wet papers over a tray to drain and dry at ambient temperature in an atmosphere free from hydrogen sulphide. Cut the dried strips into 50-mm lengths and store them in an air-tight bottle.

Rotameters for nitrogen and hydrogen with readings 0 *to* 50 *l hour*$^{-1}$.
Pure nitrogen and hydrogen in cylinders.
Silicone rubber tubing, 5 mm i.d.
E.E.L. H_2S meter (Evans Electroselenium Ltd., Halstead, Essex).
Two Chromel-Alumel thermocouples with indicating galvanometers.
Rotary gas meter, 0·5 litre per revolution.

PROCEDURE—

Preparation of adsorption tube—Assemble the complete apparatus as shown in Fig. 1, making all of the connections with silicone tubing or ground-glass joints. Purge the apparatus with nitrogen at the rate of 50 l hour^{-1} while raising the temperature of the sleeve furnace and the reduction furnace to 900 °C, by-passing the effluent gas to waste to avoid over-drying of the test paper. After purging with nitrogen for 5 minutes gradually reduce the flow; at the same time cautiously start the hydrogen flow and increase it until a rate of 20 l hour^{-1} is established when the nitrogen flow is stopped. Any connecting lines that may contain air must be purged to atmosphere with hydrogen before the hydrogen is admitted into the system. Pass hydrogen for 20 minutes with the effluent gases passing through the lead acetate paper, keeping the downstream end of the furnace tube cool with strips of moistened filter-paper. Measure the opacity of the stain obtained on the H_2S meter. If this is equivalent to more than 0·1 μg of sulphur (Note 1) continue passing hydrogen until the blank for the active carbon is constant. Reduce the temperature of the sleeve furnace to 600 °C and check the constancy of the blank again. Switch off the sleeve furnace, stop the flow of hydrogen and pass nitrogen through the apparatus at 20 l hour^{-1} until the sleeve furnace is at ambient temperature. Remove the adsorption tube and seal both ends with silicone rubber stoppers until ready for use. Stop the flow of nitrogen.

Analysis of sample—Sample the gas to be analysed by passing a suitable measured volume (Note 2) through the adsorption tube at 50 l hour^{-1}, by using a rotary gas meter downstream from the tube. Replace the absorption tube in the assembly shown in Fig. 1 and, with the lead acetate paper in position, purge the sytem for 2 minutes with nitrogen at the rate of 50 l hour^{-1}. Then reduce the flow of nitrogen to zero while starting a flow of hydrogen. When a steady flow of 20 l hour^{-1} of hydrogen is established switch on the sleeve furnace. Raise the temperature to 600 °C over a period of about 15 minutes and continue to pass hydrogen for a further 15 minutes, keeping the exit tube as cool as possible with wet filter-paper. Stop the hydrogen flow, switch off the sleeve furnace and purge the system with nitrogen as before, allowing the effluent gas to go to waste through the by-pass (Note 3). Measure the opacity of the stain on the H_2S meter, with unstained paper to zero the instrument, and calculate the concentration of sulphur in the original sample of gas from the amount of sulphur on the paper, allowing for any sulphur found in the blank test.

$$\text{Total sulphur} = \frac{\text{Micrograms of sulphur on the paper}}{\text{Volume of sample in litres}} \text{ mg m}^{-3}$$

or

$$\frac{\text{Micrograms of sulphur on the paper}}{\text{Volume of sample in litres}} \times 0{\cdot}75 \text{ p.p.m. v/v at 20 °C.}$$

NOTES—

1. The E.E.L. H_2S meter is calibrated directly in parts per million v/v of hydrogen sulphide for a gas sample of 2 foot^3. The weight in micrograms of sulphur in the stain can be calculated from the meter reading but the instrument can be readily calibrated as follows: Draw 5 ml of hydrogen sulphide from a cylinder into a gas pipette and displace it with pure nitrogen into a large polythene bag by using a rotary gas meter to measure the amount of nitrogen passed into the bag. Make the volume up to 50 litres and close the inlet of the bag with a soft rubber septum. With a gas syringe extract a measured volume from the bag and pass it through a prepared lead acetate paper that has been set up in a holder. Measure the stain produced on the E.E.L. H_2S meter. Prepare a series of suitable stains covering the range 1 to 10 ug of sulphur, then construct a graph relating micrograms of sulphur to E.E.L. meter readings.

2. The volume of gas taken should contain between 1 and 10 ug of sulphur as this is the most suitable range for the operation of the H_2S meter. If the required volume is less than 1 litre a gas syringe is to be preferred for measuring the gas passing through the active carbon.

The method can be used for the determination of total sulphur in natural gas but not more than 2 litres of the gas must be passed through the carbon. Hydrocarbons of high molecular weight present in natural gas are strongly adsorbed and reduce the capacity of the carbon to adsorb compounds of sulphur.

3. After the determination, when the adsorption tube is cool and filled with nitrogen, it should be removed and stoppered immediately as it can be used for a second test without further activation at 900 °C.

Experimental

Method B was tested on measured volumes of nitrogen doped with known amounts of dimethyl sulphide and carbonyl sulphide, either together or independently. A standard solution of dimethyl sulphide in methanol was injected through a rubber septum into the nitrogen by microsyringe; the solution used contained 0·168 g of dimethyl sulphide per 100 ml so that 10 μl contained the equivalent of 8·7 μg of total sulphur. Gaseous carbonyl sulphide was obtained from a cylinder (supplied by Air Products Ltd.) and found by mass-spectrometric analysis to be better than 99 per cent. pure. Five millilitres of the gas, measured with a gas pipette, were swept into a large polythene bag with nitrogen metered through a rotary gas meter; the volume of gas in the bag was then made up to 50 litres with nitrogen. With the aid of a 100-ml all-glass gas syringe measured volumes of gas were drawn from the bag through a rubber septum and injected into a measured stream of nitrogen, which was then passed through a silica tube packed with prepared active carbon. Between 15 and 60 ml of gas, calculated to contain between 2 and 8 μg of total sulphur, were taken from the plastic bag for a test. The analysis by method B of measured volumes of nitrogen doped with carbonyl sulphide or dimethyl sulphide, or both, is given in Table II; the sulphur was determined to the nearest microgram.

Table II

Determination of volatile sulphur compounds as total sulphur in gases by high temperature reduction in hydrogen

Dimethyl sulphide added (calculated)/ μg of sulphur	Carbonyl sulphide added (calculated)/ μg of sulphur	Volume of nitrogen/ litres	Total sulphur determined by analysis/ μg of sulphur
9	0	100	8
2	0	100	2
9	0	10	9
9	0	10	9
9	0	50	9
0	2	100	2
0	8	100	8
0	8	10	8
0	8	50	9
6	4	10	9
2	8	10	10
2	4	10	5
8	2	10	10
2	2	10	4

Determination of total sulphur in natural gas—

When natural gas was sampled by the carbon tube technique it was found that adsorption tubes prepared according to the directions given in methods A and B had a breakthrough volume of about 3 litres. High molecular weight hydrocarbons present in the gas in minor concentrations were strongly adsorbed and reduced the capacity of the active carbon to adsorb compounds of sulphur. A sample in a cylinder at 1700 p.s.i.g. was analysed by Methods A and B and again by injecting a measured volume directly into a stream of hydrogen passing through the furnace at 900 °C, as shown in Fig. 1. The resulting hydrogen sulphide was measured as a stain on lead acetate paper by the H_2S meter. A 1-litre Hamilton gas syringe was used to measure the small volumes of sample taken, which were 2 litres for the Raney nickel method (Method A), 0·2 to 2 litres for adsorption on carbon and desorption to the furnace (Method B) and 0·5 to 2 litres for the direct high temperature reduction method.

The mean of twelve results by Method A was 4·20 p.p.m. v/v of sulphur, with a standard deviation of 0·31; the mean of ten results by Method B was 4·44 p.p.m. v/v, with a standard deviation of 0·28; and the mean of four results by the direct method was 4·45 p.p.m. v/v, with a range of 0·5 p.p.m. Another sample of natural gas, which was apparently free from high molecular weight hydrocarbons, showed no breakthrough of sulphur when almost 200 litres of gas were passed through an adsorption tube. The mean of six determinations by Method A, by using volumes of sample varying between 18 and 190 litres, was 1·44 p.p.m. v/v of sulphur, with a standard deviation of 0·06.

Finally, the two methods for the determination of sulphur in gases were compared over a period of several months with an oxidation method derived from that of the Benzole Producers Conference[2] and a chromatographic method by Gibbons and Goode.[3] The distinctive feature of this chromatographic method is the flame-photometric detector in which the column effluent is passed into a hydrogen-rich flame and the ultraviolet emission at a selected wavelength is monitored by photomultiplier tube. Gas from the West Sole field that had been stenched at Easington was sampled periodically at Immingham and sent in light-alloy cylinders to Billingham where it was analysed by the four methods. Results are shown in Table III.

TABLE III

DETERMINATION OF SULPHUR IN SAMPLES OF STENCHED NORTH SEA GAS

Date	Total sulphur by gas chromatography with flame-photometric detection, p.p.m. v/v	Total sulphur by carbon tube (adsorption)		Total sulphur by oxidation method, p.p.m. v/v
		Raney nickel finish, p.p.m. v/v	Furnace method finish, p.p.m. v/v	
29.12.69	7	7·5	7·5	7
9.1.70	7·5	8	7·5	7·5
20.1.70	7	7·5	7	7
28.1.70	7	7	7	7
4.2.70	7	7	7·5	7
11.2.70	7	7	7·5	7
18.2.70	7·5	8	8	7
25.2.70	7	6	7	6
11.3.70	6	6	6	6
25.3.70	6	6	6	5
1.4.70	5	5	5	5
14.4.70	6	6	7	7

DISCUSSION

Tetrahydrothiophen was extracted from fuel gas by Colson[4] with a partition sampler containing silicone oil on Chromosorb P, and was desorbed and determined by gas chromatography. Activated charcoal was used by West, Sen and Gibson[5] to concentrate atmospheric pollutants which, after subsequent desorption by heat at 200 °C, were analysed chromatographically. Raney nickel was used at 200 °C by Jaworski and Chromniac[6] to reduce and fix the volatile combined sulphur in a gas mixture that included an excess of hydrogen. The Raney nickel was then dissolved in hydrochloric acid and the sulphide determined in the evolved gases. Adsorption of the sulphur compounds on carbon followed by treatment with Raney nickel is a convenient way of determining total sulphur in gases if no oxygenated compounds are present and, in the absence of higher boiling hydrocarbons, the method can be made sensitive and precise. It was observed in the course of these investigations that dimethyl sulphide adsorbed on to carbon could be determined more readily by Method 1, Part I, than dimethyl sulphide in solution by the same method, probably because losses by evaporation are prevented if the dimethyl sulphide is adsorbed.

Reduction with hydrogen at high temperature has been carried out by Schluter, Parry and Matsuyama,[7] who passed a gas mixture containing compounds of sulphur and an excess of hydrogen over a nickel catalyst at 1200 °C. Wronsky and Bald[8] and Struch[9] used a platinum catalyst for the reaction. This catalyst was also used at 1200 °C by Farley and Winkler[10] for the pyrolysis and reduction of liquid hydrocarbons volatilised into a stream of hydrogen, but it was necessary to saturate the hydrogen with water vapour to prevent the deposition of carbon. Method B is intended for the analysis of samples that contain only minor concentrations of hydrocarbons other than methane. The use of catalysts has been avoided in the

interests of simplicity. The results for the samples of stenched natural gas given in Table III must be treated with reserve as the composition of the gas in the cylinders may have differed from the composition of the gas in the pipeline from which the sample was taken. The most valuable characteristic of the two procedures detailed above is that the sample can be taken from places close to the main gas stream, adsorbed directly on to carbon and the analysis performed in the laboratory when convenient. Errors caused by adsorption on sample lines and containers can thus be minimised.

It will be noted that the temperature specified for the pre-treatment of the carbon is higher in Method B than in Method A. Tests showed that dimethyl sulphide was desorbed completely at 200 °C, but it was necessary to heat activated carbon to 600 °C to desorb carbonyl sulphide. A less rigorous pre-treatment is therefore permissible if the carbon is to be used to absorb non-oxygenated compounds that can be determined by the Raney nickel method. There was evidence that activated carbon sometimes contains sulphates or oxygenated sulphur compounds, which would not interfere in the Raney nickel method but must be removed if the hydrogen reduction method is to succeed. It was shown experimentally that sulphur dioxide was almost unaffected by Raney nickel but that it could be reduced rapidly under the conditions specified in Method B.

Methods involving the use of an adsorption tube packed with carbon have some distinct advantages over the other methods cited in Table III and, as the apparatus required is inexpensive and simple, they can be used in situations in which the use of more sophisticated methods would not be justified. This is particularly true of Method A, which is convenient for the determination of sulphur in stenched natural gas if only occasional tests are required. If, however, the high temperature reduction furnace is already set up and available it is more convenient to analyse natural gas by Method B as the final instrumental finish is extremely rapid.

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The Determination of Trace Amounts of Sulphide in Condensed Steam with *NN*-Diethyl-*p*-phenylenediamine

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A sensitive colorimetric method has been developed for the determination of trace amounts of sulphide in condensed steam. For precise work the colour produced by *NN*-diethyl-*p*-phenylenediamine in the presence of iron(III) ions is measured spectrophotometrically covering the range 0·5 to 100 μg of sulphide-sulphur; the standard deviations at the 100 and 1·0-μg levels are about 3 and 0·08 μg, respectively. Reasonably accurate results over the range 0·5 to 25 μg of sulphide-sulphur can be obtained "on site" by a simple visual titration of a reference solution with a methylene blue solution. The *NN*-diethyl-*p*-phenylenediamine was shown to be superior to the dimethyl homologue normally used, and its use does not appear to have been reported previously. Methods of sampling and the effect of sulphite are also discussed.

WHEN steam is used as a raw material in catalytic processes, it is necessary to ensure the absence of sulphur compounds and in particular hydrogen sulphide, which is a well known catalyst poison. Although there is no general agreement, some authors have stated that the use of sodium sulphite for the removal of oxygen from boiler feed water can give rise to the production of hydrogen sulphide in the steam.[1,2,3,4] Some raw waters may also contain hydrogen sulphide, which will appear in the steam if not removed in a water treatment plant. Steam contaminated with hydrogen sulphide would adversely affect the I.C.I. steam-reforming process and as many of our boiler waters are conditioned with sodium sulphite it was necessary to analyse samples of steam to determine hydrogen sulphide.

To carry out this programme a reliable and sensitive analytical procedure was required. A survey of existing methods suggested that one based on the formation of "methylene blue" would be the most sensitive and suitable for this purpose. Many variations of this method exist and new modifications continue to appear, all of which suggest that improvements are possible.[5 to 11] Initial studies were carried out with *NN*-dimethyl-*p*-phenylenediamine, but about this time some work had just been completed in which Palin's DPD method was used to determine chlorine in water. This method involves the use of *NN*-diethyl-*p*-phenylenediamine, which offers advantages over the dimethyl homologue, and it was felt that it might prove to be a better reagent for sulphide also. The use of *NN*-diethyl-*p*-phenylenediamine for this purpose does not appear to have been reported previously. Subsequent work showed that under our conditions it was about twice as sensitive, with adequate precision. Comparisons were made on several batches of reagent and all of the results obtained confirmed the improved sensitivity with *NN*-diethyl-*p*-phenylenediamine. After establishing a suitable laboratory procedure based on the use of this reagent, a simple field test was evolved and the effect of sulphite investigated.

EXPERIMENTAL

CONDITIONS OF TEST—

The procedure selected for examination was that given in the A.S.T.M. method,[11] as it had previously been used for effluent analysis. The method, however, was not capable of allowing less than 0·1 p.p.m. of sulphide to be determined and, as we were interested in

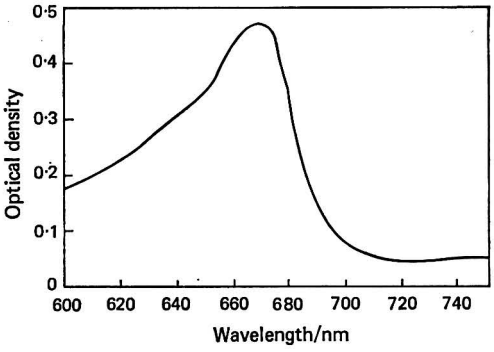

Fig. 1. Absorption curve for ethylene blue colour

concentrations down to 0·01 p.p.m. and below, some modification was necessary. Reagents were prepared in accordance with the A.S.T.M. method but sample volumes were increased to 100 ml to improve sensitivity. At this dilution, however, the precipitation of iron(III) phosphate occurred and it was decided to omit the phosphate rather than increase the acidity and incur greater risk of losing trace amounts of sulphide. Phosphate had been used in the original method to destroy the colour of the excess of iron(III) ions but under the new conditions it was unnecessary. Experiments showed that by using 1 ml of 1 per cent. *NN*-dimethyl-*p*-phenylenediamine solution and 1 ml of 10 per cent. iron(III) chloride solution in

TABLE I

EFFECT OF CONCENTRATION OF *NN*-DIETHYL-*p*-PHENYLENEDIAMINE ON FINAL COLOUR IN THE PRESENCE OF 1·0 ml OF 18 PER CENT. IRON(III) ALUM SOLUTION

Concentration per cent. w/v, of *NN*-diethyl-*p*-phenylenediamine in 50 per cent. sulphuric acid (1·0 ml used)	Net optical density		
	4·3 μg of sulphur (40-mm cell)	80 μg of sulphur (5-mm cell)	104 μg of sulphur (5-mm cell)
1·0	0·265	0·612	0·734
1·5	0·307	0·700	0·801
1·8	—	0·719	—
2·0	0·336	0·719	0·880
2·2	—	0·722	—
2·5	0·350	0·722	0·880
Blank value	0·045	0·020	0·020

TABLE II

EFFECT OF CONCENTRATION OF IRON(III) ALUM ON FINAL COLOUR IN THE PRESENCE OF 1·0 ml OF 2 PER CENT. W/V *NN*-DIETHYL-*p*-PHENYLENEDIAMINE SOLUTION

18% w/v iron(III) alum solution/ml	Net optical density	
	4·3 μg of sulphur (40-mm cell)	100 μg of sulphur (5-mm cell)
0·5	0·340	0·799
1·0	0·355	0·859
1·5	0·348	0·869
2·0	0·356	0·874
Blank value	0·045	0·020

a final volume of 100 ml, a colour was produced with sulphide which gave an absorption maximum at about 665 nm. After allowing about 15 minutes for development the colour was then stable for several hours. Small variations in the amounts of reagents used had no significant effect on the intensity of the colour and a calibration graph over the range 0 to 100 μg of sulphide-sulphur was essentially linear.

Because of the instability of dilute solutions of sodium sulphide the standard stock solution was standardised with iodine immediately prior to dilution with de-aerated water. It was also shown that the dilute working solutions were more stable if prepared in dilute de-aerated zinc acetate solution[5,7] rather than in de-aerated water alone. The final dilute solutions of sulphide contained about 0·05 per cent. w/v of zinc acetate.

The results obtained with *NN*-dimethyl-*p*-phenylenediamine under these conditions looked promising but at this juncture it was decided to investigate *NN*-diethyl-*p*-phenylenediamine as an alternative. Preliminary tests were therefore carried out under exactly the same conditions and it was found that not only did the latter give satisfactory, stable colours but that they were about twice as intense as those produced with the dimethyl homologue for given amounts of sulphide (*e.g.*, with 49 μg of sulphide values for E_{5mm} were dimethyl 0·192 at 665 nm and diethyl 0·415 at 670 nm). These promising results prompted a more detailed study of *NN*-diethyl-*p*-phenylenediamine.

As iron(III) alum was available in a purer form than iron(III) chloride and shows less tendency to hydrolyse, its use was preferred, in equivalent amounts, in all subsequent work. The absorption curve of the "ethylene blue" complex indicated a maximum at about 670 nm (Fig. 1) and this wavelength setting was used throughout. Experiments designed to study the effect of reagent concentrations were carried out and it was shown that small variations were not critical (see Tables I and II). Nevertheless, it was decided to standardise on 1·0 ml of 2 per cent. w/v solution of *NN*-diethyl-*p*-phenylenediamine in 50 per cent. sulphuric acid and 1·0 ml of 18 per cent. iron(III) alum solution. It was also established that variations in acidity or alkalinity in the sample solution equivalent to at least 5 ml of N acid or alkali caused errors of less than 5 per cent. in the colour. Although theoretical considerations[10] would suggest that the order of addition of reagents is unimportant, tests indicated that no colour was produced if the iron(III) salt was added first. Presumably the sulphide is oxidised under these conditions. Tests were finally carried out to study the effect of the time interval between reagent additions and also the stability of the final colour (see Tables III and IV). It was found that 1 minute ± 30 s between the addition of reagents was satisfactory and that full colour development occurred in 10 to 15 minutes. Thereafter the colour was stable for many hours when kept in a stoppered flask in daylight.

TABLE III

TIME BETWEEN ADDITION OF *NN*-DIETHYL-*p*-PHENYLENEDIAMINE AND IRON(III) REAGENT

Time/s	30	45	60	90	120
Net optical density for about 40 μg of sulphur (5-mm cells)	0·377	0·380	0·369	0·364	0·357
Net optical density for about 4 μg of sulphur (40-mm cells)	0·288	0·294	0·308	0·300	0·312

TABLE IV

COLOUR DEVELOPMENT AND STABILITY

Time after addition of iron(III) reagent	5 minutes	10 minutes	15 minutes	1 hour	18 hours
Net optical density for about 55 μg of sulphur (5-mm cells)	0·506	0·516	0·514	0·507	0·508
Net optical density for about 5·5 μg of sulphur (40-mm cells)	0·429	0·424	0·423	0·415	0·411
Blank on 40-mm cell	0·045	0·050	0·050	0·050	0·060

By using the conditions established, calibration graphs were prepared covering the ranges 0 to 10 and 0 to 100 μg of sulphide-sulphur in 40 and 5-mm cells, respectively. Typical results are given in Table V and confirm the linearity in agreement with the Lambert - Beer law.

TABLE V

TYPICAL CALIBRATIONS WITH *NN*-DIETHYL-*p*-PHENYLENEDIAMINE

	Net optical density		
Sulphur/μg	40-mm cell	5-mm cell	μg of sulphur per unit optical density per unit light path
1·1	0·084	—	52·5
2·2	0·164	—	53·6
4·4	0·342	—	51·5
6·6	0·516	—	53·2
8·8	0·684	—	51·3
9·9	0·756	—	52·4
14·4	—	0·136	53·0
28·8	—	0·276	52·0
43·2	—	0·408	52·8
57·6	—	0·544	53·0
72·0	—	0·676	53·1
86·4	—	0·776	55·5
97·2	—	0·870	55·7

Blank value on 40-mm cell 0·044.

EFFECT OF SULPHITE—

The main purpose of the investigation was to determine sulphide in condensed steam. Under these conditions it was considered that the only interfering substance that might be present in significant amounts would be sulphur dioxide. Because of the mutual interaction of hydrogen sulphide and sulphur dioxide under acidic conditions it was thought that the addition of the acidic *NN*-diethyl-*p*-phenylenediamine reagent might therefore give low values for hydrogen sulphide in the presence of sulphur dioxide. Factitious samples were therefore prepared in de-aerated zinc acetate solution containing various but known amounts of sulphite and sulphide. These were allowed to stand for a few minutes to simulate test conditions before the addition of the acidic *NN*-diethyl-*p*-phenylenediamine reagent. The colour was then developed in the usual way. The results obtained are given in Table VI and show that amounts up to at least 200 μg of sulphite-sulphur give an error of less than 5 per cent.

TABLE VI

EFFECT OF SULPHITE ON THE DETERMINATION OF SULPHIDE

Sulphite-sulphur/μg	Approximately 50 μg of sulphide-sulphur Net optical density (5-mm cell)	Approximately 7·5 μg of sulphide-sulphur Net optical density (40-mm cell)
0	0·495	0·564
67	0·490	0·564
101	0·485	0·564
168	0·479	0·564
235	0·475	0·559
302	0·440	0·532

As this work indicated that up to 200 μg of sulphite-sulphur could be tolerated in the sample aliquot a simple test was devised to ensure that this limit was not exceeded. In practice the sample is collected in a 100-ml stoppered measuring cylinder containing 2·0 ml of 0·00625 N iodine solution and a little starch solution or Thyodene (see Reagents, p. 206). If the volume of sample required to discharge the blue colour is less than 100 ml, this volume of sample may be taken for the analysis (see "Collection of Sample").

COLLECTION OF SAMPLE—

The collection of samples containing small amounts of hydrogen sulphide presents difficulties caused mainly by the ease with which sulphide can be lost by oxidation or volatilisation. If the "ethylene blue" method is to be used for the completion of the determination,

other problems must also be borne in mind when devising a sampling technique. Thus, the absorbing medium must stabilise the sulphide but the formation of precipitates should preferably be avoided as they may adhere to the walls of the sampling tube and vessel and not readily redissolve. Solutions of cadmium and zinc salts are commonly used to collect hydrogen sulphide, the resulting sulphides being stable. Cadmium salts, are more insoluble and their use is therefore preferable in certain circumstances. In our case, however, we considered that zinc salts were less likely to produce insoluble precipitates and were therefore preferred, the acetate being used to reduce the risk of acidic conditions developing.

Standard solutions of sulphide were prepared with dilute sodium hydroxide solution, then made slightly acidic with hydrochloric acid to "liberate" the hydrogen sulphide and transferred, by using nitrogen pressure, to a vessel containing zinc acetate solution to simulate sampling conditions. The results obtained were in good agreement with those obtained with the standard solutions before acidification and confirmed that there was no significant loss of hydrogen sulphide during the transfer. The amount of zinc acetate used was calculated to give an excess even when the maximum recommended amounts of sulphide were being determined. Gustafsson[8] has suggested that the zinc acetate should be treated with hydrogen sulphide before use to remove any interfering impurities. It was considered that this could lead to complications with high blank values and was not, in fact, found to be necessary. Nevertheless, it is recommended that blank determinations and fresh standardisations should be carried out with each new batch of reagent. Also de-mineralised water should be used in preference to water from metallic distillation units.

DEVELOPMENT OF ON-SITE METHOD—

With the conditions established above, the possibility of devising an on-site procedure was investigated. Thus, colours were produced in the usual way in 100-ml stoppered measuring cylinders by using known amounts of standard sulphide solution. Instead of measuring the colours spectrophotometrically a compensating solution was prepared in a second cylinder containing all of the reagents with de-mineralised water in place of the standard solutions. It was then found possible progressively to titrate this compensating solution visually with a standardised solution of methylene blue (1 ml being approximately equal to 10 μg of sulphur) until a colour match was obtained. The amount of sulphide that can be measured by this visual technique is limited to about 25 μg of sulphide-sulphur in a 100-ml sample volume. With larger amounts of sulphide the matching of colours becomes more difficult. By using solutions of methylene blue (standardised by comparison with colours produced with known amounts of sulphide) a series of samples was examined by the v sual and spectrophotometric methods. The results are given in Table VII.

TABLE VII

COMPARISON OF ACTUAL SAMPLES BY USING THE SPECTROPHOTOMETRIC AND VISUAL FINISH

	Sulphide-sulphur, p.p.m.					
Titration finish	0·12	0·19	0·23	0·014	0·035	0·026
Spectrophotometric finish	0·08	0·21	0·24	0·011	0·038	0·034

Bearing in mind that the titration method is regarded only as a rapid on-site method and subject to the visual interpretation of the end-point, the above results are considered to be satisfactory.

EXAMINATION OF SAMPLES—

With volumes of up to 95 ml the limit of detection is about 0·005 p.p.m. of sulphide-sulphur (Note 1). For higher concentrations the sample volume can be adjusted accordingly. Some typical results are given in Table VIII (see p. 206), sulphide having been found so far only in steam when contamination could have occurred from extraneous sources.

NOTE 1—An amount of 0·005 p.p.m. of sulphide-sulphur is equivalent to an increase in optical density of the same order as the blank (*i.e.*, about 0·04 in a 40-mm cell). This is regarded as the smallest realistic detectable change at this level of optical density.

TABLE VIII

RESULTS ON ACTUAL SAMPLES

Sample	Sulphide-sulphur, p.p.m.	
Steam exit boiler A	N.D.	
Steam exit boiler A	N.D.	N.D.
Light distillate vaporiser	N.D.	N.D.
Export steam from steam reforming plant	0·038	
Export steam from steam reforming plant	0·08	
Steam just prior to light distillate mixing point A	1·27	1·36
B	0·45	0·43
C	0·21	0·24

N.D. = not detected, *i.e.*, <0·005 p.p.m.

Where duplicate results are quoted the samples were taken from the same point within 15 to 30 minutes of each other.

SPECTROPHOTOMETRIC METHOD

REAGENTS—

De-ionised water, which has been made oxygen free by boiling and cooling under nitrogen, must be used in the preparation of standard sulphide solutions and for any necessary dilution of the sample before colour development. Other reagents may be prepared from normal laboratory de-ionised water although it may be convenient to use the de-oxygenated water prepared as above.

NN-*Diethyl*-p-*phenylenediamine solution*—Dissolve 2·0 g of *NN*-diethyl-*p*-phenylenediamine sulphate in 100 ml of 50 per cent. v/v sulphuric acid. This reagent is stable for at least 1 month, and should preferably be stored in the dark.

Ammonium iron(III) sulphate solution—Dissolve 18·0 g of $Fe_2(SO_4)_3(NH_4)_2SO_4.24H_2O$ in water. Filter if necessary to remove suspended matter and dilute to 100 ml with water.

Zinc acetate solution—Dissolve 2·5 g of $Zn(CH_3COO)_2.2H_2O$ in water and dilute to 100 ml with water.

Standard iodine solution, 0·00625 N—Prepare freshly by measuring from a microburette 6·25 ml of 0·1 N iodine into a 100-ml stoppered standard flask and diluting to the mark with water.

1 ml of solution ≡ 100 μg of sulphur.

Starch indicator solution, 0·5 *per cent. w/v*—Triturate 5 g of pure starch and 0·01 g of mercury(II) iodide with 30 ml of water in a mortar. Pour the resulting cream into 1 litre of boiling water, boil the suspension for 3 minutes, allow it to cool and settle and decant off the clear liquid. If preferred, one of the proprietary solid urea - starch mixtures such as Thyodene can be used.

Standard sulphide solution—Dissolve 2 to 3 g of analytical-reagent grade $Na_2S.9H_2O$ in water and dilute to about 1 litre. Determine the sulphide content of the solution by direct titration with 0·00625 N iodine, with the starch indicator solution.

1 ml of 0·00625 N iodine solution ≡ 100 μg of sulphur.

Immediately dilute the appropriate aliquot of this solution with water and then add sufficient zinc acetate dihydrate solution to give a solution containing 10 μg ml^{-1} of sulphur and 0·05 per cent. with respect to zinc acetate dihydrate. Standardise this solution with 0·00625 N iodine and adjust if necessary.

Dilute standard sulphide solution—Dilute 10·0 ml of standard sulphide solution to 100 ml with water and sufficient zinc acetate dihydrate solution to give a solution 0·05 per cent. with respect to zinc acetate dihydrate.

The two standard sulphide solutions are stable for at least 1 hour.

1 ml of solution ≡ 1·0 μg of sulphur.

COLLECTION OF SAMPLE—

The temperature of the sample should not be higher than 20 °C and if sampling from a flowing stream the flow-rate should be between 20 and 50 ml $minute^{-1}$. A stainless-steel cooling coil should be used.

To determine the volume of sample to be taken for analysis it is necessary to limit the amount of sulphite-sulphur present to less than 200 μg. The following preliminary tests must therefore be carried out.

To a 100-ml graduated stoppered measuring cylinder add 2·0 ml of 0·00625 N iodine and 1 ml of starch indicator solution. Collect a sample of water with a dip-tube reaching below the surface of the reagents. Note the volume at which the blue colour is discharged. This volume will contain 200 μg of sulphide and sulphite (expressed as sulphur) and not more than this volume should be taken for the test. If the colour is not discharged when 95 ml of sample have been collected, this volume can be used in the test.

PROCEDURE—

Prepare calibration graphs freshly for each new batch of reagent.

Preparation of calibration graph for the range 0 to 10 μg of sulphur—Transfer to seven 100-ml graduated stoppered measuring cylinders, each containing about 50 ml of water and 2 ml of zinc acetate dihydrate solution, amounts of dilute standard sulphide solution containing 0, 1·0, 2·0, 5·0, 7·0, 9·0 and 10·0 μg of sulphide (expressed as sulphur). Dilute to about 97 ml with water and mix gently. Add, from a pipette, 1·0 ml of *NN*-diethyl-*p*-phenylenediamine solution and mix. Allow to stand for 1 minute ± 30 s then add, from a pipette, 1·0 ml ammonium iron(III) sulphate solution. Mix and dilute to 100 ml with water.

Allow to stand for at least 10 minutes, then measure the optical density of each solution in a 40-mm cell at the wavelength of maximum absorption (about 670 nm), with water as compensating solution. Correct for the optical density of the solution containing no added sulphide and construct a calibration graph relating optical density to micrograms of sulphur present as sulphide.

Preparation of calibration graph for the range 0 to 100 μg of sulphur—Proceed in a manner similar to that outlined above for the preparation of the calibration graph for the range 0 to 10 μg of sulphur, with amounts of standard sulphide solution containing 0, 10·0, 20·0, 50·0, 70·0, 90·0 and 100·0 μg of sulphur and measure the optical density in 5-mm cells.

Determination—Collect the sample into 2 ml of zinc acetate dihydrate solution in a 100-ml graduated stoppered cylinder until the appropriate volume of sample is collected. Use a glass dip-tube with the tip below the surface of the zinc acetate solution. If necessary add water to give a total volume of 97 ml, then proceed as in "Preparation of Calibration Graph" from "Add, from a pipette, 1·0 ml of *NN*-diethyl-*p*-phenylenediamine solution. . . ." Measure the optical density of the solution in 5 or 40-mm cells, as appropriate, at the wavelength at which the preparation of the calibration graph was carried out, with water as compensating solution.

Simultaneously prepare a blank solution and a compensating solution, the former containing water instead of the sample and the latter containing the same amount of sample as used in the test but adding 1·0 ml of 50 per cent. v/v sulphuric acid in place of the *NN*-diethyl-*p*-phenylenediamine and ammonium iron(III) sulphate solutions. Determine the optical density of each of these solutions and apply any necessary correction to the optical density of the sample solution.

Read from the appropriate calibration graph the amount of sulphur present as sulphide.

CALCULATION—

$$\text{Concentration of sulphide (expressed as sulphur), p.p.m. w/v} = \frac{W}{V}$$

where W is the weight of sulphide in micrograms, found from the calibration graph, and V is the volume of sample in millilitres used in the test.

TITRIMETRIC METHOD

With this method sulphur is determined in the range 0·5 to 25 μg.

REAGENTS—

Use de-ionised water throughout as for the spectrophotometric determination described above. The following additional reagents are required.

Methylene blue stock solution—Dissolve 1 g of methylene blue in water. This stock solution is known to be stable for several weeks.

Dilute methylene blue solution—Dilute 5·0 ml of the stock solution to 100 ml with water and standardise before use.

STANDARDISATION OF METHYLENE BLUE—

Into a 100-ml graduated stoppered cylinder, containing 2·0 ml of 2·5 per cent. zinc acetate solution, add from a burette 10 ml of dilute standard sulphide solution containing 1·0 μg ml^{-1} of sulphur. Dilute to 100 ml with water. Add 1·0 ml of *NN*-diethyl-*p*-phenylenediamine sulphate reagent and mix. Wait 1 minute, then add 1·0 ml of iron(III) alum solution and mix again. Prepare a blank with water in the same way as the standard. As the colour develops in the standard add the dilute methylene blue solution from a semi-micro burette to the blank until this colour matches that of the standard. Full visual colour development occurs in the sample in about 5 minutes. Note the volume of methylene blue required for matching, then

1 ml of dilute methylene blue solution

$$= \frac{\text{Number of micrograms of sulphide taken}}{\text{Volume of methylene blue solution for the colour match}}$$

$$= \text{A } \mu\text{g of sulphide.}$$

PROCEDURE—

Collect the sample in the appropriate manner as described above and dilute to 100 ml with de-aerated water if necessary. Proceed as described in the standardisation of the methylene blue from "Add 1·0 ml of *NN*-diethyl-*p*-phenylenediamine sulphate reagent (Note 2)." Note the volume of methylene blue solution used, Y ml. This should not exceed 2·5 ml (*i.e.*, about 25 μg of sulphur) as matching is difficult above this level, then

$$\text{Concentration of sulphide (expressed as sulphur), p.p.m. w/v} = \frac{\text{Y} \times \text{A}}{\text{Volume of sample taken}}$$

NOTE 2—The sample with the colour developed may be retained and measured later by using a spectrophotometer and the sulphide determined in this way, allowance being made for the final volume and volume of sample taken.

CONCLUSION

A method has been established for the determination of traces of sulphide in condensed steam. It has been shown that *NN*-diethyl-*p*-phenylenediamine is more sensitive than the dimethyl homologue normally used.

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The Determination of Small Amounts of Cyanide in the Presence of Ferrocyanide by Distillation under Reduced Pressure

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In the analysis of effluents and waters, the customary use of lead acetate to prevent the decomposition of ferrocyanide during the distillation of cyanide is not sufficiently effective when small concentrations of cyanide (about 0·1 mg l^{-1}) are to be determined. A method is described in which the decomposition of ferrocyanide can be completely prevented by distilling off the cyanide under reduced pressure in the presence of zinc acetate. The cyanide in the distillate is determined by the pyridine - pyrazolone method.

As very small amounts of cyanide can be toxic to fish, the method for the determination of cyanide in concentrations down to about 0·1 mg l^{-1} in water and effluent samples should be as precise as possible and free from interference from other constituents. The usual procedure is to distil a large amount of an acidified sample, absorb the evolved hydrogen cyanide in a small amount of sodium hydroxide solution and finally determine the cyanide content spectrophotometrically. If the sample contains ferrocyanide, which is relatively non-toxic, the latter would partially decompose during distillation and release hydrogen cyanide, thus giving rise to positive errors. The use of lead acetate to prevent the decomposition of ferrocyanide is included in certain recommended methods of analysis of sewage and trade effluents.[1,2] These methods, however, refer to the determination of relatively large concentrations of cyanide (about 10 mg l^{-1}). Other work[3,4] in which lead acetate was used for this purpose involved milligram amounts of cyanide, which could be determined titrimetrically. Our experience has shown that lead acetate does not completely prevent decomposition of ferrocyanide and is inadequate when small amounts of cyanide are involved.

EXPERIMENTAL

Several synthetic samples were prepared containing small amounts of potassium cyanide and ferrocyanide. Distillations were carried out on these samples, after adding lead acetate to the distillation flask, and the absorbed hydrogen cyanide was determined spectrophotometrically by using a slightly modified form of the pyridine - pyrazolone method.[5] High results were obtained for each sample. Further tests were then carried out in which the lead acetate was replaced by zinc acetate, the use of which has also been recommended[6] as a way of preventing the decomposition of ferrocyanide, and although zinc acetate was much more effective than lead acetate, it did not completely prevent the breakdown. Typical results obtained with lead and zinc acetates are given in Table I.

TABLE I

KNOWN AMOUNTS OF CYANIDE AND FERROCYANIDE DISTILLED IN THE PRESENCE OF LEAD ACETATE AND ZINC ACETATE

Test No.	Distillation conditions	Ferrocyanide added/ mg l^{-1} of $K_4Fe(CN)_6$	Cyanide added/ mg l^{-1} of CN	Cyanide found/ mg l^{-1} of CN
1	With lead acetate	0	0·033	0·034
2		0·033	0·033	0·045
3		6·66	0·033	1·27
4		20·00	0	7·6
5	With zinc acetate	13·3	0	0·05
6		20·0	0·125	0·04

Various modifications were made to the procedure and finally it was found that the decomposition of ferrocyanide could be prevented by carrying out the distillation at a controlled reduced pressure in the presence of zinc acetate. Several synthetic samples were then examined by this method and good recoveries of small amounts of cyanide were obtained, even in the presence of relatively large amounts of ferrocyanide. Typical results are given in Table II. The procedure used does not prevent the decomposition of all other cyanide complexes but in some instances, *e.g.*, tripotassium pentacyanocarbonylferrate $\{K_3[Fe(CN)_5CO]\}$ and disodium pentacyanonitrosylferrate $\{Na_2[Fe(CN)_5NO]\}$, the amount decomposed is reduced.

The method has been used effectively on samples of effluents and waters during the last few years.

TABLE II

KNOWN AMOUNTS OF CYANIDE AND FERROCYANIDE DISTILLED AT REDUCED PRESSURE IN THE PRESENCE OF ZINC ACETATE

Test No.	Sample	Ferrocyanide added/ mg l^{-1} of $K_4Fe(CN)_6$	Cyanide added/ mg l^{-1} of CN	Cyanide found/ mg l^{-1} of CN
1	Distilled water	0·033	0·033	0·033
2		0·66	0·033	0·033
3		0·66	0·042	0·043
4		13·3	0	0·002
5		13·3	0·033	0·034
6		13·3	0·083	0·082
7		13·3	0·167	0·168
8		13·3	0·334	0·334
9		20·0	0·125	0·123
10		20·0	0·500	0·500
11	River water	0	0	0·004
12		1·0	0·056	0·056
13		1·0	0·054	0·055
14	Effluent containing	0	0	0·003
15	$CaCl_2$ and NaCl	1·0	0	0·002
16		1·0	0·062	0·060
17		1·0	0·062	0·063

Tests 5 to 10 were repeated on samples containing 10 per cent. w/v sodium chloride solution and similar results were obtained.

METHOD

APPARATUS—

An all-glass distillation apparatus is set up as shown in Fig. 1. The components are obtainable from laboratory suppliers, with the exception of the 250-ml absorption flask, which has been modified by means of a thimble-type extension, of about 10-ml volume, to the base of the flask. The delivery tube passes to the bottom of the thimble. This modification ensures that hydrogen cyanide evolved in the early part of the distillation passes into an an adequate column of absorption solution.

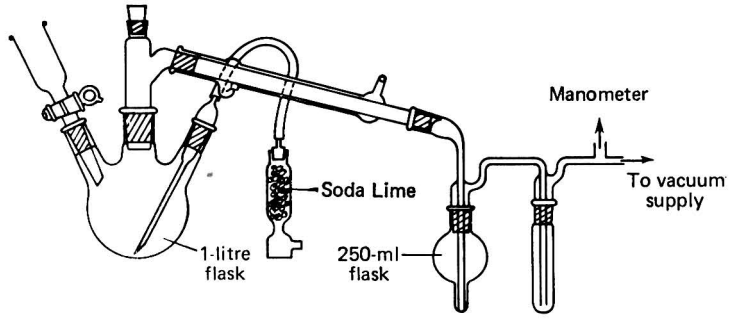

Fig. 1. Apparatus for distillation of cyanide under reduced pressure

REAGENTS—

Sodium hydroxide, 0·1 N.

Hydrochloric acid, 0·1 N.

Zinc acetate solution, 10 *per cent. w/v.*

Phenolphthalein indicator solution, 0·1 *per cent. in ethanol - water* (1 + 1).

Acetic acid solution, 0·5 *per cent. v/v.*

Chloramine T solution, 1·0 *per cent. w/v in distilled water*—This solution should be prepared daily.

3-*Methyl*-1-*phenyl*-5-*pyrazolone solution*—Dissolve 2·5 g in 500 ml of distilled water and warm the solution to 70 °C, while stirring. Allow the solution to cool in the dark, and store in a dark bottle; filter before use. Renew the solution after 5 days.

Bispyrazolone [3,3'-*dimethyl*-1,1'-*diphenyl*-(4,4'-*bi*-2-*pyrazoline*)-5,5'-*dione*] *solution*—Add 0·025 g to 25 ml of analytical-reagent grade pyridine and allow the mixture to stand in the dark, occasionally shaking it until the reagent is dissolved (about 1 hour).

Mixed pyridine - pyrazolone reagent—Filter 125 ml of 3-methyl-1-phenyl-5-pyrazolone solution into a brown bottle, add bispyrazolone solution and store in the dark. Prepare daily.

Stock standard cyanide solution—Dissolve 0·251 g of analytical-reagent grade potassium cyanide in 1 litre of distilled water containing 20 ml of 0·1 N sodium hydroxide.

Dilute standard cyanide solution—Dilute 10 ml of the stock solution to 1 litre with distilled water. This solution should be freshly prepared.

1 ml of solution contains 1·0 μg of cyanide.

PREPARATION OF CALIBRATION GRAPH—

Into a series of 50-ml standard flasks, introduce accurately measured volumes of the dilute standard cyanide solution containing 0, 2, 4, 6, 8 and 10 μg of cyanide and dilute to about 20 ml with distilled water. Add 2 drops of phenolphthalein solution, neutralise with acetic acid solution and add 0·1 ml in excess. Add 0·2 ml of chloramine T solution and allow to stand for 1½ minutes. Then add 15 ml of mixed pyridine - pyrazolone solution, mix and allow the mixture to stand for 30 minutes in the dark. Make up to 50 ml with distilled water and measure the optical density of the solution in a spectrophotometer at a wavelength of 620 nm with a 10-mm cell, with distilled water in the comparison cell.

Correct the readings for the reagent blank and plot a calibration graph relating net optical density to cyanide content.

METHOD OF CARRYING OUT THE TEST—

Introduce into the distillation flask a volume of up to 600 ml of a sample of the water or effluent, and connect the apparatus shown in Fig. 1, with the absorption flask containing 10 ml of 0·1 N sodium hydroxide and guard tube 5 ml of 0·1 N sodium hydroxide.

Titrate a separate portion of the bulk sample with 0·1 N hydrochloric acid to determine the amount of acid required to neutralise the volume of sample in the distillation flask. Add this amount of 0·1 N hydrochloric acid to the distillation flask followed by an additional 10 ml. Then add 10 ml of 10 per cent. zinc acetate solution. Connect the air inlet tube to the soda lime column and evacuate the apparatus to reduce the pressure inside to between 127 and 254 mm of mercury, while maintaining slow bubbling from the capillary of the air inlet tube. Heat the flask and boil the solution steadily until a total volume of about 75 ml is collected in the absorption flask. Stop the distillation by removing the source of heat, turn off the vacuum and allow the pressure to return to atmospheric by continuing the bubbling.

Combine the absorption and guard tube solutions and make up to volume in a 100-ml standard flask. Measure a suitable aliquot from the 100-ml standard flask (usually 20 ml) into a 50-ml standard flask and proceed with the colour development and optical density measurement as described under "Preparation of Calibration Graph."

Acknowledgement is made to the Directors of I.C.I., Mond Division, for permission to publish this paper.

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The Automated Determination of Silicon and Calcium in Portland Cement and Associated Raw Materials*

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The manufacture of Portland cement clinker is a continuous large scale chemical synthesis of specific compounds. The strength of the hydrated cement matrix in concrete is a function of the original clinker compound assemblage. Control of the production of the clinker compounds has to be related to the time of passage of materials through the rotary kiln and the conditions of processing. Continuous control of the major constituents is essential and knowledge of the effects of the variation of the constituents on the physical properties of the product is desirable.

Methods are described for the automated determination of calcium and silicon in Portland cement and associated raw materials with respect to the demands, scale and nature of the process.

THE analytical importance of the major constituents of a material can be a reflection of inherent specific properties as well as a guide to the completeness of the analysis summation. For example, in the analysis of cast iron or steels it is the minor alloying metals that are studied rather than the major constituent. However, there are other complex systems where there are several phase combinations between two elements and in these instances it may be important to know the elemental analyses with reasonable accuracy. This knowledge may help in deciding which phases are present, or in the continuous monitoring of a dynamic sytem where variables may affect the major constituents.

The major oxide constituents of a Portland cement are lime and silica, which together account for 90 per cent. of the total content. Some typical results from the samples regularly analysed in a cement works laboratory are as follows—

	Lime, per cent.	Silica, per cent.
Clay	2·0	58·0
Chalk	50·0	2·0
Raw meal	44·0	15·0
Clinker	67·0	23·0
Cement	65·0	22·0

On inspection of these results it would appear that methods having a confidence level of 0·50 per cent. for one standard deviation should suffice for the control of the plant but, in practice, much better precision than this is required. In the cement manufacturing process raw meal is calcined in a kiln into a mixture comprising four main cementitious compounds—

Molecular formula	Mineralogical abbreviation
$3CaO.SiO_2$	C_3S
β-$2CaO.SiO_2$	β-C_2S
$3CaO.Al_2O_3$..	C_3A
$4CaO.Al_2O_3.Fe_2O_3$	C_4AF

These formulae are idealised; in practice, the silicate minerals contain interstitial aluminium, magnesium and titanium oxides, alkalis, etc. Early cement microscopists called C_3S solid solution alite, C_2S belite and the iron complex is now known as ferrite. Cement manufacture is basically a continuous large-scale synthesis of these compounds. The time of passage of the raw material through the rotary kiln may be of the order of 2 hours, and the analytical control system has to be devised with this in mind.

* Presented at the symposium on "Accurate Methods of Analysis for Major Constituents," organised jointly by the Society for Analytical Chemistry and the Analytical Section of the Royal Dutch Chemical Society, London, April 3rd to 4th, 1970.

The development of strength of a cement matrix is a function of the compound assemblage, the relative influence of each of the four main phases being shown in Fig. 1.

It must be stressed that strength calculations based on the hydraulic activity of chemically pure cement compounds must be modified as a result of the inclusion of minor elements in solid solution. Compound composition is used as a guide to the potential strength of the finished product and analyses at a rate of at least one per hour are required.

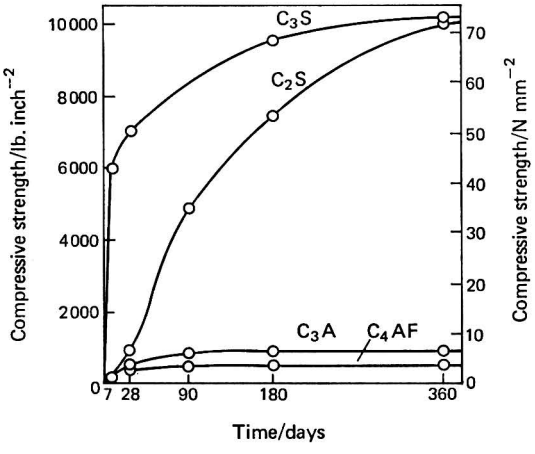

Fig. 1. Development of strength of pure cement compounds[1]

EFFECT OF ANALYTICAL ERRORS—

Consider the introduction into a kiln of a carbonaceous raw meal having the chemical composition: silica 15·0 per cent., aluminium(III) oxide 3·0 per cent., iron(III) oxide 1·5 per cent. and lime 43·5 per cent.

Then, under ideal conditions and assuming no ash absorption from the fuel, a clinker will be produced containing: silica 21·3 per cent., aluminium(III) oxide 4·6 per cent., iron(III) oxide 2·3 per cent. and lime 67·0 per cent., basing the transposing factor (slurry to clinker) on

$$\frac{100}{(100 - \text{ignition loss at } 1400\ ^\circ\text{C})}$$

From this chemical analysis it is possible to calculate a theoretical compound composition of the clinker provided the percentage of unreacted or free lime present is known. Hence, the following compound formation can be postulated by using the method enunciated by Bogue[2]: alite 58·8 per cent., belite 23·4 per cent., C_3A 8·3 per cent., ferrite 7 per cent. and free lime 1·5 per cent.

Assuming no error has occurred in the determination of aluminium and iron, then 0·5 per cent. error in the silica analysis gives rise to a 6 per cent. error in the alite estimate, and 0·5 per cent. error in the lime analysis leads to a 3 per cent. error. Thus the coupled effect of these two errors leads to underestimation of the alite by more than 9 per cent. and overestimation of belite by the same amount.

Alite[1] has a 7-day strength of 40·68 N mm^{-2} and a 28-day strength of 49·30 N mm^{-2} and belite[1] has corresponding strengths of only 0·69 and 6·90 N mm^{-2}, other phases contributing very little to the strength of the cement. Although belite ultimately develops a strength equal to that of alite, it is early strengths that are of importance to the construction industry. The influence of variation of alite content upon compressive strength is shown in Table I.

Thus, the 0·5 per cent. analysis errors can lead to strength estimations that may be about 4 N mm^{-2} low at 28 days. For control of the plant, calculations of compound composition to ± 2 per cent. of alite are required and it is therefore necessary to use analytical techniques capable of determining silica to $\pm 0{\cdot}07$ per cent. and lime to $\pm 0{\cdot}1$ per cent. for one standard deviation.

Assumptions made in the Bogue calculation are included in this study where a multi-component system (silica - aluminium(III) oxide - iron(III) oxide - lime) is being considered under specific conditions. It is assumed that all the iron, aluminium and silicon and the calcium not existing as uncombined lime or as calcium sulphate will be combined as C_3S, C_2S, C_3A and C_4AF. The particle-size distribution of the ground compound assemblage in the presence of gypsum is a further contributor to the strength of a hydrating matrix, mainly from the aspects of kinetics and efficiency of hydration.

TABLE I

INFLUENCE OF VARIATION OF ALITE CONTENT UPON COMPRESSIVE STRENGTH

Alite content,* per cent.	7-day strength/ Nmm^{-2}	28-day strength/ Nmm^{-2}
56·8	28·96	39·10
53·5	27·65	37·62
50·8	26·34	36·61
47·0	25·24	35·10

* The belite content will increase relatively as the alite content decreases.

SAMPLE DISSOLUTION FOR AUTOMATED ANALYSIS—

Fuse the sample[3] with a strong alkali in a gold - palladium crucible and leach with hot water. Pour the alkaline suspension into a solution of sufficient hydrochloric acid to dissolve the calcium and iron hydroxides and, after cooling, dilute to a known volume (500 ml).

The range of lime and silica to be measured together with the sample weight required for the various materials is given below in Table II.

TABLE II

SAMPLE WEIGHT FOR MATERIALS ANALYSED

	Sample weight/g	Lime, per cent.	Silica, per cent.
Clay	0·250	0 to 6	48 to 64
Chalk	1·000	30 to 53	0·5
Raw meal	1·000	42 to 54	12 to 16
Cement and clinker	0·600	63 to 68	20 to 27

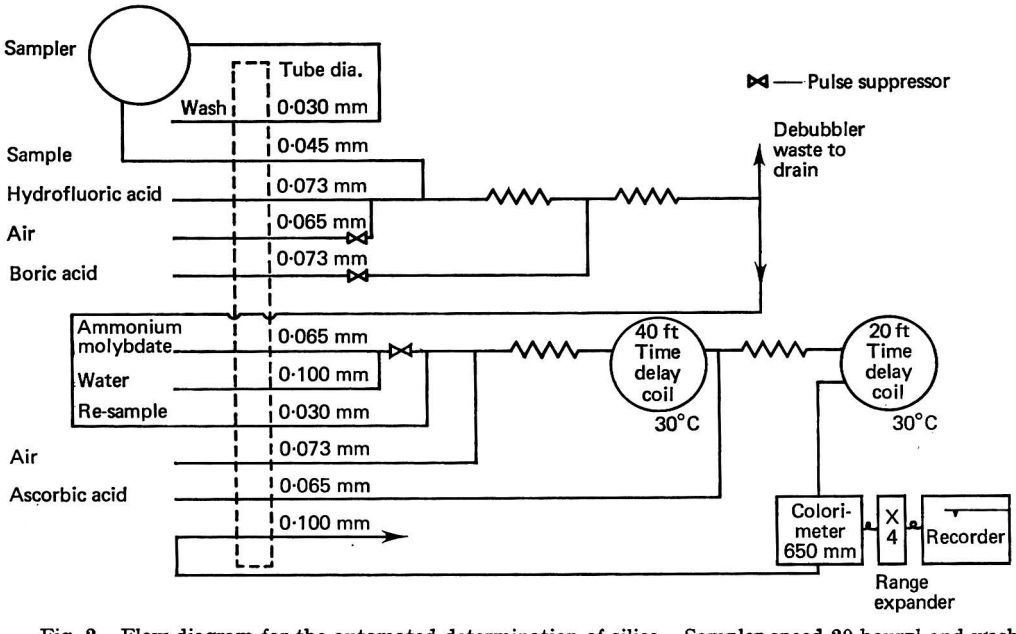

Fig. 2. Flow diagram for the automated determination of silica. Sampler speed 20 $hour^{-1}$ and wash ratio 1:2

AUTOMATED DETERMINATION OF SILICA

For the determination of silica an automated molybdenum blue method has been developed; the required reactions are given by the flow system (Fig. 2).

REAGENTS—

Wash reagent—An aqueous solution of 0·22 g l^{-1} of pure precipitated silica prepared by fusion (as for samples).

Hydrofluoric acid—A solution of 5 ml of 40 per cent. hydrofluoric acid in 1 litre of water.

Boric acid—A saturated aqueous solution (approximately 50 g l^{-1}).

Ammonium molybdate—A solution containing 2·5 g in 1 litre of 0·3 per cent. v/v sulphuric acid.

Ascorbic acid—An aqueous solution containing 10 g l^{-1} of ascorbic acid.

METHOD—

The addition of hydrofluoric acid to the flowing sample stream complexes the iron, decomposes any polymerised silicic acids and converts them to a silicofluoride complex. Excess of hydrofluoric acid is then complexed by excess of boric acid, which also decomposes the silicofluoride ion to give fluoroborate and silicate ions. A yellow silicomolybdic complex is formed by adding acidified ammonium molybdate and the product is finally reduced to the molybdenum blue complex by ascorbic acid. Phosphate will interfere but in practice (considering a sample sequence at an individual plant) phosphate content is almost constant and is very low; in the United Kingdom it does not exceed 0·05 per cent. If the phosphate is known to have a detectable variation, any interference that it may cause can be suppressed by the addition of citric acid.[4]

Initially the analyser was set up to give an optimum performance over the range 0 to 16 per cent. of silica and the charts obtained looked very promising, but a 1 per cent increment of silica concentration was represented by only 2·5 per cent. transmission and interpretation gave errors outside the control limit. For raw meal analysis the range measured is 12 to 16 per cent., so washing with water was replaced by washing with a solution containing silica equivalent to 11 per cent. in the sample. The base-line was set at 98 with the full colour development from 11 per cent. of silica passing through the flowcell and peaks were obtained

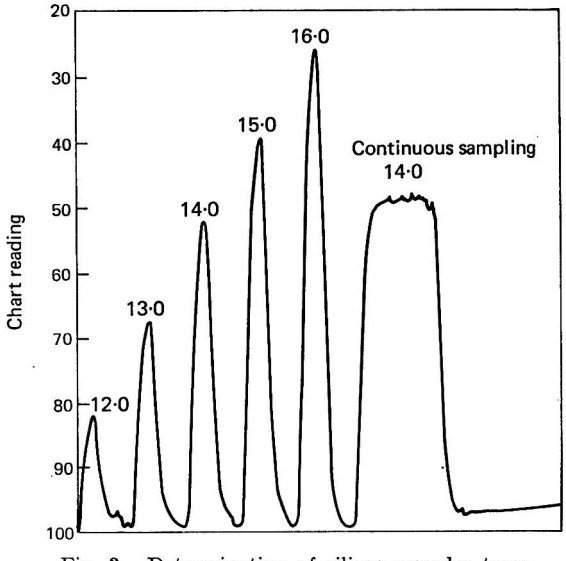

Fig. 3. Determination of silica: recorder trace

for the standards. In this way the resolution improved to 3·5 per cent. transmission per 1 per cent. increment. A ×4 range expander was then employed to boost the resolution to 14 chart transmission units per 1 per cent. of silica. By using this technique the peaks shown in Fig. 3 are obtainable, the base-line varying from peak to peak by less than 1 chart division (±0·035 per cent. of silica). If peaks are allowed to reach their maximum then a precision of ±0·035 per cent. of silica can be obtained but, in practice, the sampling time is insufficient to allow a state of equilibrium in the system. However, ±0·04 per cent. can be achieved for one standard deviation and this precision meets the requirements of the method; Fig. 4 shows the calibration graph. Having developed this system it was extended to the analysis of clays, chalks and clinkers.

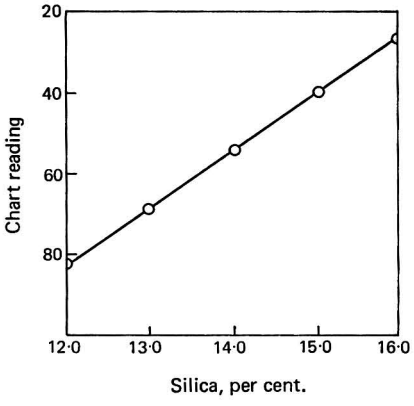

Fig. 4. Determination of silica: calibration graph

For clay analysis 0·25 g of sample is used instead of 1 g (see Table II) so that the 12 to 16 per cent. standards represent a range from 48 to 64 per cent. in the clay, and similarly 0·6 g of cement and clinker is taken to measure the range 20 to 27 per cent. For chalk samples a method of standard addition can be used by adding the equivalent of 11 per cent. of silica to the solution before diluting to volume. In this way the standards range from 1 to 5 per cent.

Cement samples have been analysed by the AutoAnalyzer and by the reference B.S.I. method.[4] Each sample was analysed three times by each technique and thirty samples in all were used. The average deviation between the two methods for the ninety results was 0·03 per cent. and the standard error between the mean of the triplicates 0·06 per cent.

Automated determination of lime

For the determination of lime up to the 70 per cent. level normal colorimetric procedures were discounted because a 1 per cent. increment of lime would be represented by less than 0·5 per cent. transmission. An EDTA titration would seem to be better for this analysis, but in order to achieve a faster output of results, a system that is a compromise between titrimetry and colorimetry has been developed.

In Fig. 5 (see p. 218), a manifold for the analysis of lime over the range 0 to 4 per cent. is shown.

Reagents—

Triethanolamine—A 100 ml l^{-1} aqueous solution.

Buffer, pH 13—An aqueous solution containing 10 g l^{-1} of sodium tetraborate *plus* 20 g l^{-1} of sodium hydroxide.

Colour reagent—A methanolic solution containing 0·75 g l^{-1} of glyoxal bis-2-hydroxyanil.

Standard EDTA—An aqueous solution containing 8·35 g l^{-1} of EDTA disodium salt (dihydrate) standardised against B.C.S. 372.

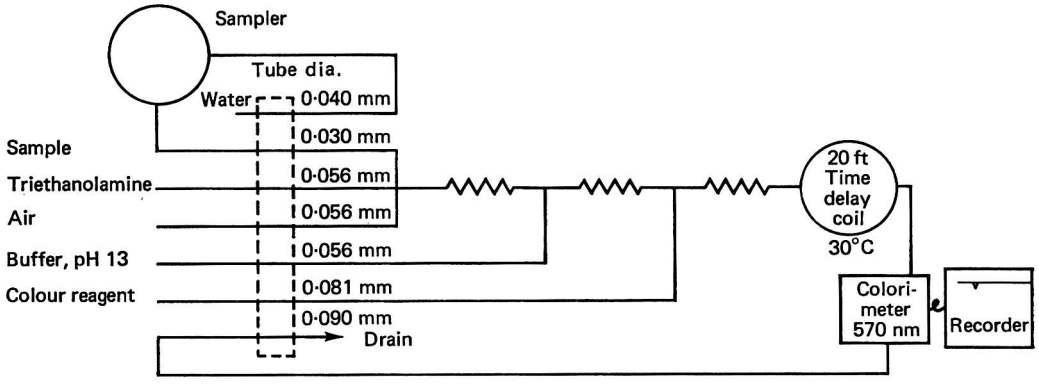

Fig. 5. Flow diagram for the automated determination of lime. Sampler speed 20 hour^{-1} and wash ratio 1:2. Colour reagent glyoxalbis-2-hydroxyanil, which must pass only through Solvaflex tubing

METHOD—

Triethanolamine solution is added to the sample to complex iron and the pH is adjusted to 12·6 by a buffer. A 1 per cent. glyoxal bis-2-hydroxyanil (bis-(2-hydroxyphenylimino)-ethane) solution in methanol[3] is then added to produce a red 1:1 complex with calcium and the absorbance measured at a wavelength of 570 nm. Fig. 6 shows a typical recorder trace for lime and Fig. 7 illustrates a calibration chart.

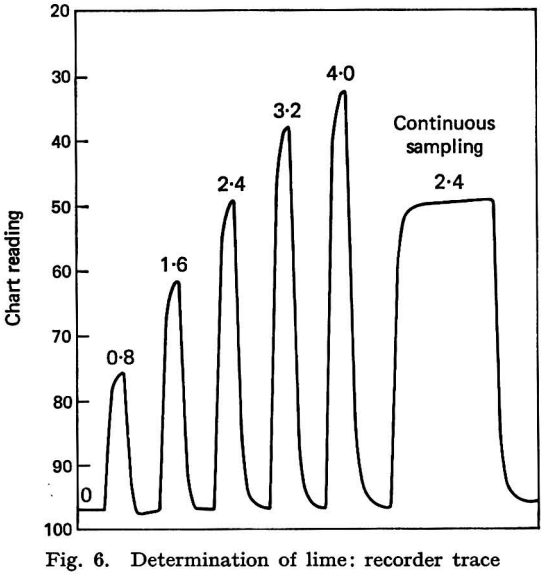

Fig. 6. Determination of lime: recorder trace

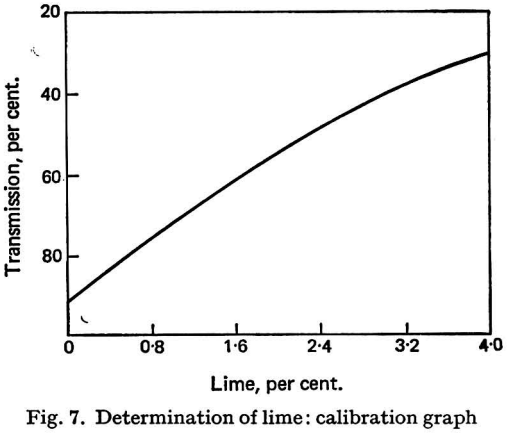

Fig. 7. Determination of lime: calibration graph

A calculated amount of EDTA is added to test solutions so that not more than 4 per cent. but greater than zero lime is left uncomplexed in solution. The mixture is then analysed by the AutoAnalyzer for excess of lime content.

The EDTA solution is made such that 1 ml is equivalent to 1 per cent. of lime in 50 ml of test solution. So, for raw meal analyses, 42 ml of EDTA (43 to 45 per cent. of lime being determined) are added to 50 ml of test solution, the volume is diluted to 100 ml with water and the mixture is analysed for excess of lime.

The percentage of lime in the sample is then 42 *plus* the chart reading. From Table II, cements and clinkers range from 63 to 68 per cent. of lime, but because 0·6 g of sample is used to prepare a test solution and not the 1-g standard, the measuring range becomes 37·8 to 40·8 per cent. of lime. To 50 ml of cement solution 38 ml of EDTA solution are added before dilution to 100 ml with water. The excess of lime is determined and

$$\text{Percentage of lime} = \frac{38 + \text{chart reading}}{0{\cdot}6}$$

Chalk samples range from 30 to 53 per cent. lime content but at a factory site the samples fall into two categories called high and low chalks. Low chalks contain 30 to 34 per cent. of lime and high chalks 49 to 53 per cent. To 50 ml of chalk solution 30 or 49 ml of EDTA, whichever is appropriate, is added before dilution to 100 ml with water and measurement of excess of lime. The lime content is then the volume of added EDTA *plus* the chart reading.

Clays contain less than 6 per cent. of lime so in this case the neat test solution is analysed directly. As 0·25 g is used and the solution is not diluted further, the results are obtained by multiplying the chart reading by two.

Results obtained for cements agree well with results from the B.S.I. method.[4] Triplicate analyses of 30 samples showed an average deviation between methods of 0·05 per cent. with a standard error of 0·13 per cent.

Conclusion

The two methods outlined and also methods[3,5] for aluminium(III) oxide, iron(III) oxide, sulphur trioxide and free lime[5,6] have been used for plant control of two factories for the past 3 years. Samples are analysed at hourly intervals and a considerable improvement in quality stability has been achieved. Some thought has been given to an automated digestion system so that the analyser can be operated in the plant itself, and when this problem has been overcome the system may then find a place in many more factories.

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Determination of Calcium by Radiochemical Replacement

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The determination of calcium ions in solution by radiochemical replacement of silver-110 in labelled solid silver oxalate, cobalt-60 in labelled cobalt oxalate and manganese-54 in labelled manganese oxalate has been examined. A one-to-one replacement was observed with manganese oxalate. The technique can be used to determine 2·5 to 100 μmole ml^{-1} (100 to 4000 μg ml^{-1}) of calcium, and the lower limit is reduced to 16 μg ml^{-1} by using a 50 per cent. methanol solution. Magnesium interferes to only a small extent. Each determination takes less than 5 minutes, and the precision is ±2 per cent.

Relatively few methods are available for determining calcium ions in the micromolar range. Those based on the precipitation of calcium oxalate, which involve gravimetry or titrimetric determination of excess of added oxalate with potassium permanganate, are limited by the solubility of calcium oxalate, which is 6 mg l^{-1} at 18 °C.[1] Titrimetric determination with EDTA, with murexide as indicator, flame photometry and atomic-absorption spectrophotometry can also be used. This work describes attempts to replace labelled cations from several solid oxalates by calcium ions. It appears that manganese oxalate labelled with manganese-54 may be a useful reagent for determining calcium in solution.

Experimental

Reagents—

Cobalt oxalate labelled with cobalt-60—Five grams of the dihydrate were prepared by adding a slight excess of oxalic acid solution to a solution of cobalt(II) nitrate containing cobalt-60 and neutralising it with sodium hydroxide solution.[2] The pink suspension was boiled and centrifuged, and the precipitate thoroughly washed and dried. The specific activity was such that 1 count s^{-1} corresponded to 1·35 μmole of cobalt.

Silver oxalate labelled with silver-110—Five grams of the anhydrous salt were prepared by adding a slight excess of oxalic acid solution to a solution of silver nitrate containing silver-110, and nearly neutralising it with sodium hydroxide solution. After centrifugation the white solid was washed and dried, and it was found that 1 count s^{-1} corresponded to 14·7 μmole of silver.

Manganese(II) oxalate labelled with manganese-54—Five grams of the dihydrate were prepared by adding a slight excess of oxalic acid solution to a solution of manganese acetate containing 50 μCi of manganese-54, boiling and neutralising it with sodium hydroxide solution. After centrifugation the white solid was washed and dried at 110 °C to give the pink anhydrous salt,[3] with very slight surface decomposition to a brown oxide; 1 count s^{-1} corresponded to 465 μmole of manganese. The work of Coltman[4] should be consulted for another mode of preparation.

Calcium nitrate—Standards were prepared by dissolving 1·0009 g of analytical-reagent grade calcium carbonate in the minimum amount of 2 M nitric acid and neutralising any excess of acid with sodium hydroxide solution before making the volume up to 100 ml. Other standards were prepared by appropriate dilution.

Magnesium acetate—Standards were prepared from an 0·1 M solution containing 2·145 g of analytical-reagent grade magnesium acetate tetrahydrate in 100 ml of water.

PROCEDURE—

About 4 g of labelled oxalate were transferred to a filtration tube, 15 cm long and 1 cm i.d., in which it formed a column about 2·5 cm high resting on a sintered-glass disc. Four-millilitre volumes of water were passed through the column by using a filter pump until the specific activity of the eluates was constant, which was usually achieved after four to six volumes had passed through. The eluates were transferred to tared counting vials, weighed and counted in a well-type sodium iodide crystal connected to a single-channel analyser. In each instance the analyser controls were adjusted to give the maximum count-rate by focusing on the main γ-energy of the radionuclide concerned. The counts, after correction for any weight losses and background counts, were compared with those obtained from 4 ml of a solution containing a known weight of the solid oxalate dissolved in nitric acid.

As soon as the water eluates reached a constant specific activity, the column was tested by eluting with various dilutions of calcium nitrate. It was found that constant specific activity of the eluate was rapidly achieved with each new solution applied. As a sample could be filtered in 2 to 4 minutes and counted in 100 s, each replicate analysis could be carried out in less than 5 minutes. Time of contact does not appear to be important.

RESULTS AND DISCUSSION

The solubilities and solubility products of the oxalates of silver, barium, calcium, cobalt, manganese, magnesium and strontium are given in Table I. There are some disagreements in the literature with regard to these values, but the orders of magnitude of the solubilities quoted are probably correct.

TABLE I

SOLUBILITIES AND SOLUBILITY PRODUCTS OF SOME OXALATES

Formula	Solubility/mg l^{-1}	Temperature/°C	Reference	Solubility product, K
$Ag_2C_2O_4$	37·8	21	5	$7·72 \times 10^{-12}$
BaC_2O_4	112	18	6	$2·47 \times 10^{-7}$
CaC_2O_4	6·0	18	1	$2·19 \times 10^{-9}$
CoC_2O_4	34·6	25	7	$5·54 \times 10^{-8}$
MgC_2O_4	345	25	8	$9·43 \times 10^{-6}$
MnC_2O_4	270	18	9	$3·57 \times 10^{-6}$
SrC_2O_4	46·1	18	10	$6·89 \times 10^{-8}$

According to the values given in this table, the order of replacement of ions from their oxalates should be: $Ag^+ > Ca^{2+} > Sr^{2+} > Co^{2+} > Ba^{2+} > Mn^{2+} > Mg^{2+}$.

The experimental replacement of silver, cobalt and manganese ions from their oxalates by calcium ions is shown in Figs. 1 and 2. All points are the means of at least three readings agreeing to within ± 2 per cent.

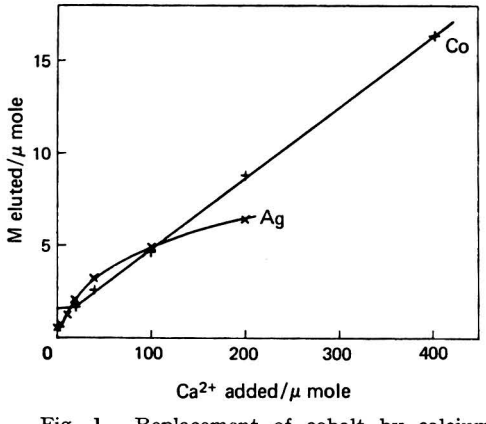

Fig. 1. Replacement of cobalt by calcium in $^{60}CoC_2O_4$ (+) and of silver by calcium in $^{110}Ag_2C_2O_4$ (×)

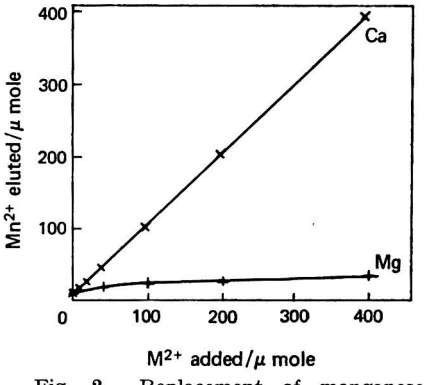

Fig. 2. Replacement of manganese by calcium (×) or magnesium (+) in $^{54}MnC_2O_4$

With the labelled silver oxalate, the replacement was both inefficient and non-linear. When the results in Fig. 1 were re-plotted with $[Ag^+]^2$ instead of $[Ag^+]$ as the y-axis, a linear graph was obtained, as expected on theoretical grounds; with the labelled cobalt oxalate, the replacement was linear but inefficient. Only about 4 per cent. of the theoretical amount of cobalt was replaced by the percolating calcium ions; however, with the labelled manganese oxalate, the replacement was both linear and efficient. Virtually 100 per cent. of the theoretical amount of manganese ion was replaced by calcium ions. This salt was therefore studied further to ascertain its suitability for determining calcium.

REDUCTION OF BLANK VALUE—

The blank for the labelled manganese oxalate column was found to be 2·65 μmole ml^{-1} by using distilled water. It was found that addition of up to 70 per cent. by weight of ethanol to 0·1 M calcium nitrate did not result in precipitation of the salt. Blanks run with 25 and 50 per cent. v/v methanol were 1·00 and 0·37 μmole ml^{-1}, respectively. Hence it should be possible to determine calcium in the range 0·4 to 100 μmole ml^{-1} (16 to 4000 μg ml^{-1}) by this technique.

pH RANGE—

Manganese oxalate is soluble in dilute mineral acids but not in acetic acid. Hence the technique should not be used at pH below 4·0 and, if possible, sample readings should be calibrated with standards at the same pH.

INTERFERENCES—

As most oxalates other than those of the alkali metals are insoluble, many cations will be expected to interfere in the determination of calcium by this technique. This interference has been tested for the element magnesium, which often accompanies calcium in nature. The results, shown in Fig. 2, indicate that replacement by magnesium is both non-linear and inefficient, so that magnesium interference is unlikely to be serious. For example, 400 μmole of magnesium displace as much manganese-54 as does 16 μmole of calcium.

It should be noted that the results of these replacement experiments disagree by several orders of magnitude with quantitative predictions from the values given in Table I. It is not clear whether this disagreement is caused by the inaccuracy of the solubility values in Table I, or by the rate of exchange between calcium ions and solid oxalates being so slow that equilibrium is scarcely approached under the experimental conditions used here. These disagreements do not, however, affect the practical utility of the technique.

The technique was tested by using standard kale.[11] One gram of kale powder was wet ashed with perchloric acid - nitric acid (1 + 1) and taken to dryness. The residue was dissolved in 100 ml of water and brought to pH 7 with a few drops of sodium hydroxide solution. Four samples of this solution were passed through the manganese oxalate column. The calcium content of the kale was found to be 40 140 $\pm$ 1 080 mg kg^{-1}, which compares favourably with the mean literature value[11] of 40 000 mg kg^{-1}.

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Microdetermination of Mercury in Biological Samples

Part II.* An Apparatus for Rapid Automatic Determination of Mercury in Digested Samples

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Urine samples that have been cold-digested by potassium permanganate - sulphuric acid mixture overnight are analysed in apparatus consisting of an automatic sample changer, pumps for transferring the sample solution to a purgation tower and adding tin(II) chloride solution, which reduces mercury(II) to metallic mercury, and a spectrophotometer. The mercury vapour is liberated from the solution in the tower by a flow of nitrogen and then taken through the absorption cell in the spectrophotometer where the light absorption at a wavelength of 253·7 nm is continuously recorded. After completion of the purgation, the mercury-free solution is transported back to the original tube in the sample changer by reversing the pumps, and the next analysis is started. The mercury content in the sample is calculated from standard graphs drawn from results with known amounts of mercury. Sixty digested samples, each containing 1 ml of urine, are analysed in about 2 hours without any manual work or supervision. In each sample about 1 ng of mercury can be detected, but normally the working range for urine samples is 0 to 400 ng ml^{-1} of mercury(II). The analysis can be applied to biological or any other samples that can be digested in a similar manner.

In a previous paper,[1] one of us described a rapid method for the determination of mercury in digested urine, which was based upon the reduction of mercury(II) to the metallic state by tin(II), followed by removal of mercury vapour by purging with air and cold-vapour atomic-absorption determination of mercury. The speed of analysis was fairly high, and the detection limit about 2 ng of mercury in a 1-ml urine sample.

At present, there is a great demand for trace determination of mercury in large series of samples of water, food, urine, blood and organs. To reduce the cost of such analyses it is essential to find methods which can bring down the amount of work needed to a minimum. Therefore, we have worked out an automatic method for the determination of mercury in samples that have been wet digested. This method depends upon the same basic principle as the manual method described in the first paper. The main features of the apparatus constructed by us can be described as follows—

(*i*) The sample solution is at first transported by a pump to a reactor tower for purgation. At the same time a second pump transports tin(II) chloride solution from a storage vessel to the sample tube, whence it is transported to the purgation tower by the first pump, rinsing the tubing as it goes.

(*ii*) Purgation of the reduced sample solution mixture containing freshly formed metallic mercury is carried out by a nitrogen stream in the tower through its sintered-glass filter bottom.

(*iii*) When purgation is finished, the remaining mercury-free solution is transported back to the original tube by reversing the pump motor.

(*iv*) An automatic sample changer is used to shift to a new sample after purging and back-flushing of the preceding sample.

* For particulars of Part I of this series, see reference list, p. 229.

Experimental

Apparatus—

A rough schematic diagram of the apparatus is given in Fig. 1. The main parts of the apparatus are described in detail below.

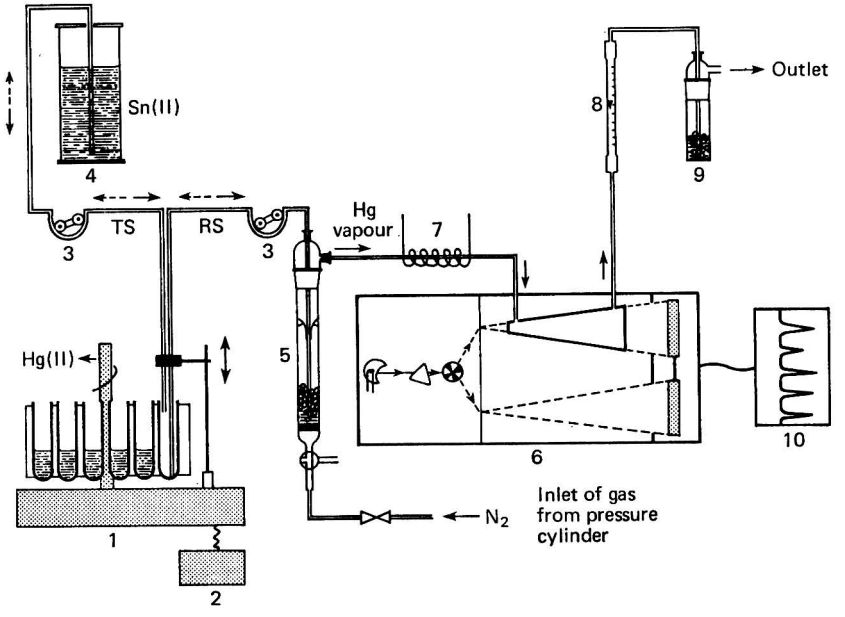

Fig. 1. The complete apparatus: 1, automatic sample changer holding 60 samples; 2, electronic timer; 3, reversible peristaltic pumps on the same axis; 4, reduction solution; 5, reactor (purgation tower); 6, double-beam spectrophotometer with mercury lamp; 7, heating wire; 8, flow-meter; 9, permanganate scrubber; and 10, recorder

The sample changer—Samplomat, manufactured by Struers, Copenhagen, Denmark. This has a turntable with test-tube holders for 60 sample tubes, and a suction tip (of Teflon tubing), which periodically is lowered into one of the sample tubes for sucking the sample solution to the purgation tower and is raised again before the turntable moves to bring the next sample into position. The Samplomat was modified in a few respects by us. On the main axis, rotated at a speed of 2 r.p.m. by a synchronous motor, there were originally two cams regulating the movement of the turntable and suction tip. An additional cam was attached to the same axis controlling a switch to reverse the pump motor (see under The pumps and Figs. 2 and 3). Further, three parallel switches mechanically controlled by the axis were installed, of which two started a timer and the third disconnected the circuit, including the pump motor and Samplomat. This disconnection took place exactly at the same moment as the flow of solution was to be reversed towards the test-tube ($p^- \rightarrow p^+$, Fig. 3).

The timer—Constructed by N. Bjerker. The timer contains a 2-μF condenser, the charging time of which can be regulated between 0 and 140 s by a variable resistor. When the charge has reached a certain voltage (the voltage of a glow lamp), the condenser discharges and, at the same moment, the timer short-circuits the disconnection switch and the cycle continues.

The pumps—Two identical peristaltic pumps (Multifix, R. Grave AB., Solna, Sweden) were used for the transport of sample solution and of tin(II) solution. The pump housing diameter was 56 mm and the pumps were mounted on the same axis, being driven by a reversible a.c. shunt motor via a 1:18 worm gear. The motor ran off a 220-V supply and had a maximum speed of 3 000 r.p.m. Its direction of rotation could be reversed by interchanging the poles and its speed could be adjusted by means of a potentiometer (Fig. 2).

The suitable working range for the pumps was 100 to 250 r.p.m. For the transport of the solutions, silicone rubber tubing was preferred, as it was superior to other types in wear resistance. The inner diameter of the tubing used was 2·0 mm for the sample solution and 1·5 mm for the tin(II) solution. (The tubes are marked RS and TS, respectively, in Fig. 1.) A circuit diagram showing the connections between the Samplomat motor, the timer and the pump motor is reproduced in Fig. 2.

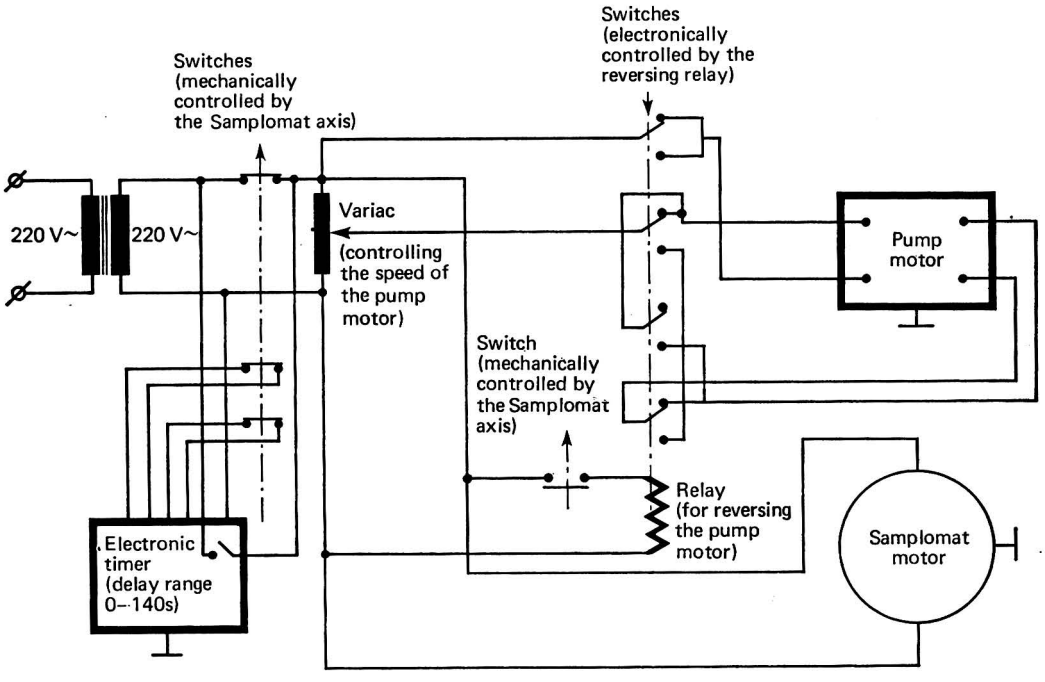

Fig. 2. Circuit diagram showing the connections between the Samplomat, the pump motor and the timer

Purgation tower—This was made of Pyrex glass tubing (length 150 mm, diameter 18 mm) having a G4 sintered-glass filter at the bottom and a ground-glass joint at the top. A small plastic funnel was inserted into the tower to serve as a collector of droplets. Nitrogen was introduced through the bottom, and the flow was adjusted by a valve. The inlet and outlet tubing for the sample solution reached down to the filter, thus minimising the residual volume after the solution had been back-flushed by the pump.

Spectrophotometer—A double-beam Hitachi Perkin-Elmer 124 spectrophotometer with a Beckman mercury discharge lamp 2260 as light source and a specially constructed 8-cm gas cell made of Plexiglass with quartz windows was used. To minimise dead space, this cell was made to fit the light-beam through the cell compartment. The cell volume was about 8 ml. Alternatively, an ordinary 10-cm cylindrical cell can be used, but the gas volume needed for complete removal of mercury vapour is then increased, so that the peak heights become slightly smaller. A heating wire is wound round the tubing before the cell inlet to warm the gas stream in order to avoid condensation in the cell.

Recorder—A Servogor RE511 was used. For routine urine analysis, a scale range of 20 or 10 mV was used. If smaller amounts of mercury were to be determined, the range was set at 5 or 2 mV.

OPERATING PRINCIPLES OF THE APPARATUS—

A diagram demonstrating the movements of the suction tip and the turntable of the Samplomat and of the pumps during the working cycle is given in Fig. 3 (see p. 226). In the

starting position, the suction tip is raised and the pumps are not working. When the apparatus is switched on, the pumps start (direction p^-, Fig. 3) and the suction tip falls down into the sample tube in position. One pump sucks the sample solution through tubing RS (Fig. 1) to the purgation tower, while the other pump sucks tin(II) solution through tubing TS (Fig. 1) to the sample tube. The length of TS is so adjusted that the tin(II) solution reaches the sample tube at the same moment as the last residue of the sample solution is sucked up into the suction tip. During the next few seconds tin(II) solution is transported to the purgation tower via the sample tube, rinsing tubing RS from sample solution as it goes.

After about 6 s of flow in direction p^-, the poles of the pump motor are reversed. At the same moment, however, the main current to the Samplomat and to the pump motor is automatically disconnected. The pumps now stop, and the suction tip is left in its lowest position (Fig. 3). During the stop period, mercury is removed from the solution in the tower by the nitrogen stream. The length of this period can be adjusted with the aid of the timer (up to 140 s).

During the next period, the pump motor is reversed (direction p^+, Fig. 3). The sample solution is then back-flushed through RS from the tower to its original test-tube in the Samplomat. At the same time the tin(II) solution in TS is pumped back into the storage vessel, so that TS is empty when the next cycle starts. After about 10 s of p^+, the suction tip starts to rise. When it has reached its top position, the pump motor is reversed again ($p^+ \rightarrow p^-$) and the turntable moves to bring the next sample in position. The cycle is then repeated. The length of the cycle is 30 s, excluding the stop period caused by the timer.

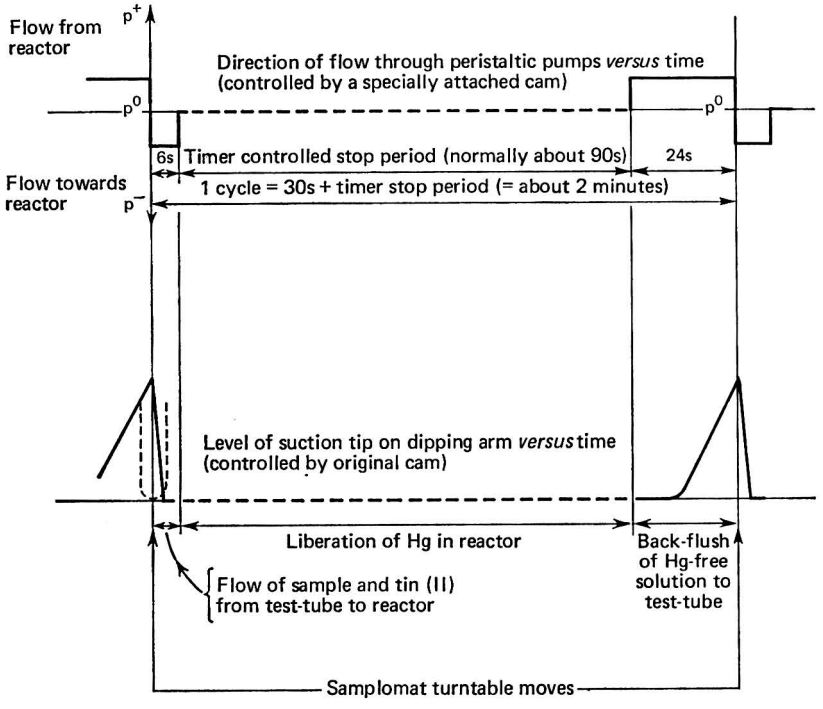

Fig. 3. The connections between the flow directions of the pumps and the movements of the sample changer

REAGENTS—

All chemicals used were of analytical-reagent grade.

Digestion solution—Mix 150 ml of potassium permanganate solution (6 per cent. w/v) with 20 ml of concentrated sulphuric acid immediately before use.

Hydroxylammonium chloride solution—Dissolve 50 g of hydroxylammonium chloride in 100 ml of water. Before use, shake it with a solution of dithizone in chloroform to remove traces of mercury. The solution is stable.

Tin(II) chloride solution—Dissolve 20 g of tin(II) chloride dihydrate in 1 litre of water containing 40 ml of concentrated sulphuric acid. This solution must be freshly prepared, as a precipitate forms in it after a few days.

Mercury stock standard solution—Dissolve 678 mg of mercury(II) chloride in 0·1 N sulphuric acid, and make the volume up to 1 litre. This solution contains 500 μg ml^{-1} of mercury. It remains stable for a long time when stored in a polythene bottle. A working standard solution containing 10 μg ml^{-1} of mercury is prepared from the stock solution before each series of analyses. From this solution the amounts needed for a standard curve are taken out with a Hamilton microlitre syringe and are mixed with a 1-ml urine sample from persons that have not been exposed to mercury. We prefer a urine standard to the water standard previously used, because the matrix may influence the peak heights because of differences in viscosity, etc.

PROCEDURE—

Digestion—Pipette 1·0 ml of urine sample or standard solution into a 100 × 16-mm tube. Add 1·5 ml of digestion solution, mix by swirling and leave the sample, loosely covered by a plastic stopper, overnight at room temperature. Next day, hydroxylammonium chloride solution is added dropwise, with swirling, until the solution is colourless and clear.

Analysis—Switch on the spectrophotometer and the mercury lamp 30 minutes before the start of the analysis. Adjust the nitrogen flow to about 100 ml minute^{-1} with the aid of the flow-meter and needle valve. Place the sample tubes into the turntable of the sample changer and fill the storage vessel with tin(II) chloride solution. Then, set the timer at a suitable pause time (generally 90 s), switch on the recorder (20 mV) and start the chart paper (running at 2 mm minute^{-1}).

Start the analysis by throwing the main switch controlling the sample changer and the pump motor. The apparatus then analyses the whole series of samples automatically without supervision. A special stopper that starts an alarm bell when the last sample is analysed may be placed in the turntable.

Calibration—The calibration graph is constructed and the peak heights are evaluated as described for the manual method.[1] However, the calibration graph is less linear than with the manual method (Fig. 4). It begins to deviate from a straight line at about 100 ng of mercury per sample. Because the reproducibility is good even on the curved part of the graph, the practical working range is 0 to 400 ng of mercury.

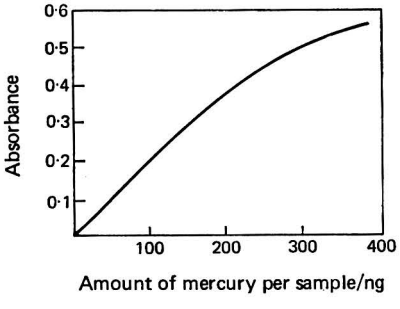

Fig. 4. Calibration graph for mercury contents of 0 to 400 ng per sample

RESULTS AND DISCUSSION

The apparatus has been used for the routine determination of mercury in urine with very good results. A series of 60 digested samples can be analysed in about 2 hours without supervision. There is no memory effect between samples. The standard deviation for single

determinations was determined at the 100-ng and 300-ng levels by analysing a number of identical samples. At 100 ng, we found it to be ± 2 per cent. (calculated on 22 runs), and at 300 ng, ± 3 per cent. (on 23 runs).

A comparison was made between the automatic and manual methods with 32 urine samples (see Fig. 5). The correlation was very good ($r = 0{\cdot}99$) and the regression coefficient (the slope of the regression line) was 0·98.

The reagent blank corresponds to about 1·5 ng of mercury. When working at a recorder range of 2 mV, the smallest detectable amount of mercury is about 1 ng per sample.

Some variations in the absorbance were observed when determining the same amount of mercury on different days. The reason for this is not known. It is therefore necessary to construct a new calibration curve for each series of analyses.

In practice, the apparatus may be equipped with a much simpler spectrophotometer than the double-beam Hitachi 124 used by us. Even a mercury detector without monochromator, *e.g.*, the Kruger or the Incentive HGM2300, could be used. However, the more stable the instrument the smaller is the amount of mercury that can be detected, and the narrower the spectral band used, the smaller is the interference from other absorbing substances.

In addition to urine, the apparatus can determine mercury in any kind of sample that can be digested with the amount of permanganate - sulphuric acid used for 1 ml of urine. For example, the standard procedure is sufficient to digest 0·05 ml of blood. As the average mercury content of blood from non-exposed persons is about 5 ng g^{-1}, it is difficult to reach the normal blood mercury level with permanganate digestion although slightly elevated levels from exposed persons are easily determined. We are at present trying to analyse larger volumes of blood by using other digestion solutions. The results of this work are to be published later.

We have also shown that compounds with Hg–C bonds can be digested and quantitatively determined with this procedure by determining the mercury content of methylmercury, ethylmercury, phenylmercury and the two diuretics Diurgin and Salyrgan.

Magos and Cernik[2] have recently published a method for mercury determination in urine without previous digestion. This method is based on the increased reduction potential of tin(II) in alkaline solutions that makes it possible to reduce the mercury attached to sulphydryl groups of proteins directly. However, the mercury of Hg–C bonds is not determined without digestion. Obviously this suggests the possibility of distinguishing between Hg–C and Hg–S bonds. Unfortunately, this direct method needs the addition of an antifoaming agent for the purgation. When trying this technique on our apparatus, the antifoaming agent sometimes formed a thin layer on the cell windows, so disturbing the light absorption. However,

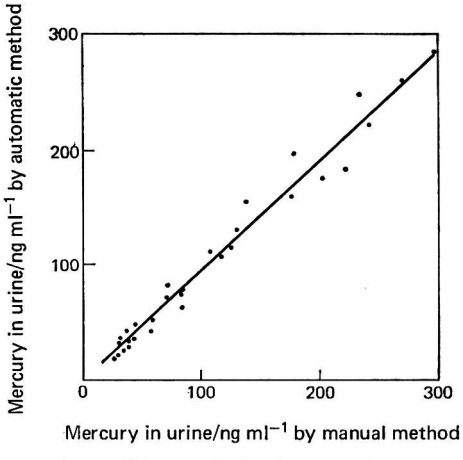

Fig. 5. The correlation between the manual and automatic methods in analysing urine samples. Correlation coefficient, r, = 0·99

an advantage of the alkaline method is that bromide and iodide do not interfere. In acid solution, because of the formation of complex ions with higher reduction potentials,[1] the presence of these ions prevents the reduction of mercury(II) ions.

The proposed method has been found to work well with different kinds of samples. It permits mercury determinations in the nanogram range to be carried out at high speed and minimum cost. It is our intention to extend its application to further types of samples.

We thank the Swedish Board for Technical Development for generous financial support, Miss K. Liljeros and Mrs. L. Hagstedt for technical assistance, Mr. N. Bjerker, who made the electrical components, and Mr. C.-E. Enquist, who carried out the mechanical workshop work.

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NOTE—Reference 1 constitutes Part I of this series.

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Propylene Carbonate Extraction of Tris(pentan-2,4-dione)-iron(III) from Aqueous Solution: Application to the Spectrophotometric Determination of Iron

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Orange tris(pentan-2,4-dione)iron(III) is extracted from aqueous solution into propylene carbonate at pH 4·0 to 9·0. Distribution coefficients range from 23·9 to 116, depending on the ionic strength and pH of the aqueous phase. Relative standard deviations of the spectrophotometric methods developed are 1·52 per cent. or less and these methods are applicable to the routine determination of 56 to 391 μg of iron. One of the methods was applied to the determination of iron in wrought aluminium alloy. The importance of using non-toxic solvents in analytical chemistry is emphasised.

PROPYLENE carbonate (4-methyl-1,3-dioxolane-2-one) is an excellent solvent for the extraction of ferroin-type iron(II) complexes from aqueous solution.[1] The solvent has the characteristics normally desired in an extractant: it is colourless, denser than water, non-toxic, almost odourless, and has little tendency to form emulsions. Propylene carbonate is partially soluble in water; however, aqueous solutions can be rapidly and predictably saturated with the solvent.[1] At 24 °C the solubility of propylene carbonate in water is 0·254 g ml^{-1} and in 2·7 M sodium chloride 0·125 g ml^{-1}.

It is noteworthy that with the increased concern over the nature and quality of man's environment, little solicitude has been expressed regarding the routine use of highly toxic solvents, such as benzene, diethyl ether, chloroform, carbon tetrachloride and nitrobenzene, as extractants or solvents in analytical chemistry. Propylene carbonate is non-toxic and consequently is preferred as an extractant to these toxic solvents.

Of the many reagents proposed for the spectrophotometric determination of iron, the ferrointypes are unquestionably superior and almost universally used to determine iron(II). It may on occasion, however, be advantageous to determine iron as iron(III), in which event the ferroin-type reagents are of little use. Lieser and Schroeder,[2] for example, used pentan-2,4-dione (acetylacetone) to extract iron(III) from iron(II). It is also possible that solvent extraction may be desirable, even when relatively large amounts of the desired constituent are present and concentration of that constituent is not necessary. Extraction from coloured solutions and from possible interferences are typical examples of this situation. The proposed method can therefore be used to advantage when it is desirable to determine relatively large amounts (about 50 to 400 μg) of iron(III) colorimetrically and when iron is to be determined in complex matrices. The small molar absorptivity (about 3 000) of the tris(pentan-2,4-dione)-iron(III) chelate permits its use for the former and the relatively specific nature of the method permits its use for the latter. In those instances when total iron is to be determined it is, of course, necessary to incorporate an oxidising agent into the method.

Pentan-2,4-dione was chosen as an extraction - chromogenic chelating agent for this study because it forms coloured chelates with only a few other metal ions and is readily available.

The extraction of iron(III) as the pentan-2,4-dione complex has hitherto been accomplished in two ways. The complex has been extracted into solvents such as carbon tetrachloride, chloroform, 4-methylpentan-2-one, xylene, benzene[3] and butyl acetate,[4] and has also been extracted into pentan-2,4-dione itself, the solubility of which in water is 0·172 g ml^{-1} at 20 °C.[5]

Experimental

Apparatus—

A Perkin-Elmer, Model 202, recording spectrophotometer and a Corning, Model 10, pH meter with conventional electrodes were the principal instruments used. Separating funnels with Teflon plugs and plastic stoppers were used for the extractions.

Reagents—

Pentan-2,4-dione—Purify commercial-grade material as recommended by Morrison and Freiser.[6]

Water—Pass distilled water through a mono-bed ion-exchange column composed of Dowex 50W-X2 resin in the hydrogen form and Dowex 1-X1 resin in the hydroxide form.

Propylene carbonate—Vacuum-distil technical-grade material in all-glass apparatus.

Standard iron solution—Prepare a $1{\cdot}80 \times 10^{-2}$ M (1000 μg ml^{-1}) stock solution by dissolving electrolytic iron in hydrochloric acid. Prepare daily a $1{\cdot}80 \times 10^{-4}$ M (10 μg ml^{-1}) iron solution from the stock solution.

Phosphate buffer, pH 6·84—This was M with respect to both disodium hydrogen and sodium dihydrogen orthophosphates.

Acetate buffer, pH 4·75—This was 2 M with respect to both acetic acid and sodium acetate.

Interferences—Prepare solutions of possible cation interferences from the chloride, nitrate or sulphate salts by dissolving the pure metal in the appropriate acid; prepare possible anion interferences from sodium and potassium salts.

Other chemicals used were of analytical-reagent grade.

Recommended procedure—

Place an aqueous solution of the sample expected to contain 1·50 to 6·00 μmole of iron, if phosphate buffer is used, or 1·00 to 7·00 μmole of iron, if acetate buffer is used, into a suitable separating funnel. (The stopcock bore and stem of the funnel should have previously been rinsed with 2 to 3 ml of propylene carbonate.) Adjust the volume to about 60 ml and ensure complete oxidation of the iron to iron(III) by adding 1 ml of saturated chlorine water or 3 per cent. hydrogen peroxide solution. Add 1 ml of pure pentan-2,4-dione, adjust the pH to between 4 and 9 with phosphate or acetate buffer, and add 2 to 10 ml of saturated sodium chloride solution. Saturate the resulting solution with propylene carbonate (12 to 15 ml), adding sufficient excess to give about 7 ml of extractate. Shake the separating funnel for about 1 minute and allow the phases to separate, while gently swirling intermittently. Drain the lower phase into a 25-ml calibrated flask and rinse the stopcock bore and funnel stem with 1 ml of propylene carbonate. Extract again with 5 and 3-ml portions of propylene carbonate and rinse after each extraction. Make up to final volume with propylene carbonate and measure the absorbance in 1-cm cells at 440 nm.

Results and discussion

Determination of iron in aluminium alloy—

To test the general utility of the proposed method, iron was determined in United States National Bureau of Standards (N.B.S.) standard sample 85B wrought aluminium alloy. Approximately 0·6-g portions of the alloy were weighed into 100-ml calibrated flasks, dissolved in 7 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid, and the solutions made up to volume. Iron was determined in 10-ml aliquots by using the recommended procedure (with chlorine water and acetate buffer). The propylene carbonate was added immediately after the addition of the pentan-2,4-dione, buffer and salt to prevent the precipitation of tris(pentan-2,4-dione)aluminium(III). The results are shown in Table I. Similar results were obtained when the pentan-2,4-dione was added after saturation with propylene carbonate.

Table I

Determination of iron in N.B.S. standard sample (85B wrought aluminium alloy)

Run	1	2	3	4	5	Average
Iron, per cent.	0·231	0·236	0·227	0·226	0·224	0·229

N.B.S. analyses: Reported 0·24 per cent., average 0·236 per cent., range 0·23 to 0·24 per cent.

PARAMETERS AFFECTING THE METHOD—

Effect of hydronium ion concentration—The recommended procedure was used to extract 4·50 μmole of iron. The pH was adjusted to various values with sodium hydroxide and hydrochloric acid solutions (Fig. 1). Acetate (pH 4·75) and phosphate (pH 6·84) were suitable buffers. Phosphate buffer caused precipitation when large amounts of cations such as aluminium(III) and magnesium(II) were present.

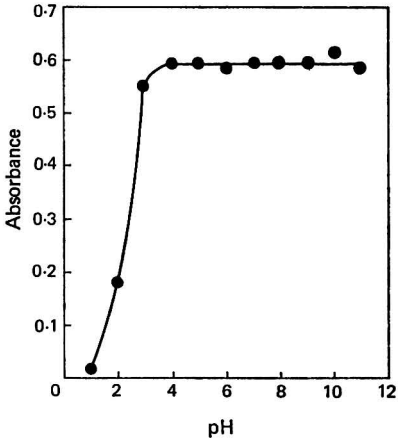

Fig. 1. Effect of pH on the sensitivity of the method

Effect of ionic strength—Into each of several separating funnels were placed 4·50 μmole of iron, the volume of solution was adjusted to about 60 ml, and 1 ml each of chlorine water and pure pentan-2,4-dione were added. Various combinations of buffers and salt solutions were added and sufficient propylene carbonate was added to give a 5 to 10-ml extract. The funnel was shaken for 3 minutes, and allowed to stand until the aqueous phase was completely clear (2 to 3 hours). The absorbance of the aqueous phases was measured in 5·00-cm cells and the absorbance of the propylene carbonate phases in 1·00-cm cells. Distribution coefficients are indicated in Table II.

TABLE II

EFFECT OF IONIC STRENGTH ON THE DISTRIBUTION COEFFICIENT AT 25 °C

Buffer	pH	Salt	$K_D = \frac{[Fe(aa)_3]_{P.C.}}{[Fe(aa)_3]_{Aq.}}$
10 ml of acetate	4·75	None	23·9
10 ml of acetate	4·75	10 ml of saturated NaCl	46·0
10 ml of acetate	4·75	10 ml of saturated $MgCl_2$	51·3
10 ml of acetate	4·75	0·05 mole of Na_2SO_4	116*
10 ml of triethanolamine HCl	6·84	10 ml of saturated NaCl	40·9
10 ml of phosphate	6·84	2 ml of saturated NaCl	35·3

* The slightly cloudy extract was clarified by adding several drops of ethanol.

Effect of oxidising agents—The recommended procedure was used. In one experiment 4·50 μmole of iron were extracted after adding 1 ml of saturated chlorine water; in another 4·50 μmole of iron were extracted after adding 1 ml of 3 per cent. hydrogen peroxide solution. The absorbances of the extracts were identical and higher than the absorbance of an extract that was obtained for 4·50 μmole of iron when no oxidising agent was added.

Effect of pentan-2,4-dione concentration—The recommended procedure was used and 4·50 μmole of iron were extracted after the addition of various amounts of pure pentan-2,4-dione; addition of 10, 1·0 and 0·5 ml resulted in identical absorbances.

Effect of iron concentration—Phosphate buffer (10 ml) was incorporated into the recommended procedure and 0 to 9·0 μmole of iron were extracted. In another series of experiments, 10 ml of acetate buffer were incorporated into this procedure and 0 to 7·2 μmole of iron were extracted. The wavelength of maximum absorbance and molar absorptivities were determined in the usual way. The method of Ringbom[7,8] was used to determine optimum concentration ranges for the methods and standard deviations were calculated for these ranges. For the recommended procedure incorporating the phosphate buffer, λ_{max} was at wavelength 440 nm and the value for ϵ was $3{\cdot}20 \times 10^3$. The optimum concentration range was 1·50 to 6·00 μmole (84·0 to 335 μg) of iron and the relative standard deviation over this range 1·00 per cent. Beer's law was obeyed over the range 0·900 to 9·00 μmole of iron. For the recommended procedure incorporating the acetate buffer, λ_{max} was at wavelength 440 nm and the value for ϵ was $3{\cdot}26 \times 10^3$. The optimum concentration range was 1·00 to 7·00 μmole (56·0 to 391 μg) of iron and the relative standard deviation over this range was 1·52 per cent. Beer's law was obeyed over the range 0·900 to 7·20 μmole of iron.

Effect of time on the extracts—The absorbance of an extract was measured daily over a 6-day period and no change in absorbance was observed. Propylene carbonate extracts of the complex showed no signs of deterioration over the period of the investigation (3 months).

Effect of diverse ions on the method—The recommended procedure was used incorporating 150 μg of iron, the diverse ion, 1·0 ml of chlorine water, 1·0 ml of pure pentan-2,4-dione, 10 ml of phosphate buffer and 2 ml of saturated sodium chloride solution. The results shown in Table III are given with the more serious interferences listed first.

TABLE III

EFFECT OF DIVERSE IONS ON THE METHOD

150 μg of iron and phosphate buffer

Diverse ion	Added/μg	Error, per cent.	Diverse ion	Added/μg	Error, per cent.
Titanium(IV)	1000	−26·3	Chromium(III)	1000	− 2·2
Titanium(IV)	220	− 5·9	Zinc(II), cadmium(II), mercury(II)	1000 each	+ 1·8
Chromate	1000	−17·3	Magnesium(II), calcium(II), strontium(II)	1000 each	+ 1·8
Chromate	330	− 5·9	Barium(II)	1000	+ 1·8
Tin(IV)	1000	−13·2	Copper(II)	1000	+ 1·5
Tin(IV)	430	− 7·4	Aluminium(III)	1000	+ 0·6
Arsenic(III)	1000	− 9·4	Fluoride, bromide, iodide	1000 each	0·0
Arsenic(III)	750	−21·1	Sulphate	1000	0·0
Arsenic(III)	530	−10·6	Nitrate	1000	0·0
Arsenic(III)	407	−14·7	Perchlorate	1000	0·0
Arsenic(III)	300	− 2·3	Acetate	1000	0·0
Bismuth(III)	1000	− 7·9	Lithium(I), potassium(I), ammonium	1000 each	0·0
Bismuth(III)	700	−14·7	Cerium(IV)	1000	0·0
Bismuth(III)	384	− 7·9	Vanadium(V)	1000	0·0
Bismuth(III)	300	− 2·9	Manganese(II)	1000	0·0
Tin(II)	1000	− 5·9	Nickel(II)	1000	0·0
Silver(I), lead(II)	1000 each	+ 5·8	Antimony(III)	1000	0·0
Molybdenum(VI)	1000	− 3·5			
Arsenic(V)	1000	+ 3·5			
Cobalt(II)	1000	− 3·0			

CONCLUSIONS

The proposed method should be useful for the routine extraction and determination of fairly large amounts of iron (84 to 335 μg with phosphate buffer, or 56 to 391 μg with acetate buffer). The method is not only convenient and fairly specific, but is safe and pleasant to use.

Of the possible interferants studied, attention should be drawn to the erratic effects on the method of arsenic(III) and bismuth(III). Although some interference is indicated for aluminium(III), copper(II) and chromium(III), their presence in N.B.S. standard sample 85B wrought aluminium alloy caused no apparent interference. The alloy contained 3·99 per cent. of copper and 0·211 per cent. of chromium.

When the method is used to determine iron in biological material, following wet ashing with mixtures of nitric and perchloric acids, two situations should be noted. If the perchloric

acid is not removed by evaporating to fumes with sulphuric acid, an unusually large amount of propylene carbonate is required to saturate the aqueous phase, and the resulting cloudy propylene carbonate extract must be clarified by the addition of 1 to 2 ml of ethanol. It has been previously noted[1] that the solubility of propylene carbonate in water is increased by the presence of perchlorate ion. Secondly, the presence of large amounts of sulphate (about 0·05 mole) causes cloudy propylene carbonate extracts that must be clarified by the addition of 1 to 2 ml of ethanol.

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Levamisole: Its Stability in Aqueous Solutions at Elevated Temperatures

Part I. Isolation and Identification of Decomposition Products Formed in Aqueous Solutions of Levamisole Stored under Nitrogen and Oxygen at 100 °C

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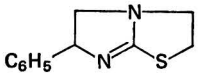
Solutions of *l*-tetramisole (levamisole) buffered over a pH range of 2 to 8 were stored under nitrogen and oxygen at 100 °C. The decomposition that occurred was detected by thin-layer chromatography. The decomposition products were isolated and their structures elucidated by standard instrumental procedures.

LEVAMISOLE is the *l*-isomer of 6-phenyl-1,2,3,5,6-tetrahydroimidazo[2,1-*b*]thiazole—



It is an anthelmintic drug and knowledge of its stability in the presence of water is an essential pre-requisite to formulation. Preliminary experiments have shown that aqueous solutions of levamisole buffered over a pH range of 2 to 8 and stored at 100 °C under nitrogen or oxygen decompose. The purpose of this work was to identify the decomposition products and ultimately develop an assay specific for levamisole to facilitate further stability studies.

EXPERIMENTAL

GENERAL—

Solutions were prepared at pH values of 2·2, 3·0, 4·0, 5·0, 6·0 and 8·0 by using a double-strength McIllvaine's buffer system[1] in a mixture of 0·4 M disodium hydrogen phosphate and 0·2 M citric acid. The reagents used were of AnalaR quality; the oxygen and nitrogen (White Spot) were from the British Oxygen Company. Measurements of pH were made at 23 °C with a glass electrode and E.I.L. model 23A direct-reading pH meter.

PREPARATION OF SOLUTIONS STORED UNDER NITROGEN—

Buffer solutions containing 0·5 per cent. of levamisole were prepared in an atmosphere of nitrogen in water previously boiled to expel dissolved gases. Borosilicate glass ampoules of 5-ml capacity were filled with these solutions, immediately sealed and stored at 100 ± 1 °C for 5 days.

PREPARATION OF SOLUTIONS STORED UNDER OXYGEN—

A number of 10-ml samples of 0·5 per cent. buffered levamisole solutions were distributed into 25-ml borosilicate glass ampoules, sealed under oxygen and stored as described above.

PROCEDURE FOR EXAMINING SOLUTIONS BY USING THIN-LAYER CHROMATOGRAPHY—

Silica-gel plates (Merck G.F. 254, 20 × 20 × 0·03 cm) were activated prior to use by heating for 20 minutes in an oven at 115 °C. Then 200 μg of the drug were applied to the plates, which were subsequently developed over a 15-cm solvent run with a system of chloroform - methanol - ammonium hydroxide (90 + 10 + 1) in a tank lined with filter-paper. The spots were located by using three methods: first, ultraviolet irradiation (at a wavelength of 254 nm); second, spraying with iodoplatinate solution (equal volumes of 6 per cent. potassium iodide solution and 0·3 per cent. platinum chloride solution); and third, spraying with 1 per cent. ninhydrin solution in ethanol followed by heating at 120 °C for 20 minutes.

ISOLATION OF DECOMPOSITION PRODUCTS FROM SOLUTIONS STORED UNDER NITROGEN—

At pH 2·2 to 3, two decomposition products, R_F 0·3 and 0·7, were produced, and only one (R_F 0·7) over the remainder of the pH range. The former was located by ultraviolet irradiation at 254 nm and gave a purplish-pink spot on spraying with ninhydrin. There was no response with iodoplatinate. The latter was detected by ultraviolet irradiation at 254 nm and gave a white spot with iodoplatinate. There was no response with ninhydrin. The solution at pH 8 was extracted with chloroform, and the extract was washed with water, dried over anhydrous sodium sulphate and concentrated in a Rotavap at 35 °C. The oily residue, when examined by thin-layer chromatography, gave two spots, one at R_F 0·7, and a faint one at R_F 0·4 (levamisole).

The presence of an amine group in the spot at R_F 0·3 was demonstrated by its reaction with ninhydrin. To obtain sufficient material for identification, 500 mg of levamisole were dissolved in 20 ml of N hydrochloric acid, transferred to a borosilicate glass ampoule sealed under nitrogen and heated for 34 days at 100 °C. (Other studies at pH 2 had demonstrated that the hydrolysis of levamisole was complete after 34 days at 100 °C.) The solution was washed with chloroform and evaporated to dryness on a Rotavap at 70 °C, after which the residue was dried over phosphorus(V) oxide at ambient temperature *in vacuo*. Thin-layer chromatography confirmed that the residue was the component at R_F 0·3, with a faint trace of the components at R_F 0·4 and 0·7. Additional confirmation was obtained by a second thin-layer chromatographic system, benzene - acetone - ammonia solution (sp.gr. 0·880), (50 + 50 + 1).

ISOLATION OF DECOMPOSITION PRODUCTS FROM SOLUTIONS STORED UNDER OXYGEN—

Over the pH range studied a thin-layer chromatographic examination showed two major decomposition products, at R_F 0·55 and 0·8. The component at R_F 0·3 was found after decomposition at pH 2·2 to 3·0 with a faint spot of the component at R_F 0·7. This was again confirmed by chromatography in the benzene - acetone - ammonia solution system referred to previously.

The component at R_F 0·8 was isolated from solution at pH 7·9 by the thin-layer chromatographic procedure already described, on a plate from which all impurities had been removed by three washings with methanol, and across which 0·5 ml of the solution had been streaked. After development the band at R_F 0·8 was removed, transferred to a No. 2 sintered-glass microfilter and eluted with 5 ml of methanol. The methanol was subsequently removed by warming to 40 °C in an atmosphere of nitrogen, the residue being kept for spectrophotometric studies.

The thin-layer chromatographic studies suggested that the spots at R_F 0·55 and 0·7 were possibly related as the former was very pronounced in solutions stored under oxygen but not under nitrogen, whereas the converse applied to the component at R_F 0·7. This can be explained if it is assumed that a trace of oxygen is present in solutions stored under nitrogen. As the spot at R_F 0·7 was identified as a thiol (see Results) it is reasonable to expect that it would oxidise to the disulphide, which might be the component at R_F 0·55. To confirm this, oxygen at ambient temperature was slowly bubbled through a solution at pH 7 that had been previously stored at 100 °C under nitrogen for 15 hours. The heavy white precipitate obtained was removed by filtration through a Whatman No. 1 filter-paper and the residue, after drying over phosphorus(V) oxide *in vacuo* at 40 °C, was twice recrystallised from ethyl acetate and dried as previously described. Thin-layer chromatography showed a component at R_F 0·55 and a faint spot (only detectable after spraying with iodoplatinate) at R_F 0·7.

IDENTIFICATION OF DECOMPOSITION PRODUCTS—

Infrared spectra were obtained on dispersions in potassium bromide by using a Unicam SP100 or Perkin-Elmer 457 grating infrared spectrophotometer, and nuclear magnetic resonance spectra were recorded by use of a Varian A60 or H.A. 100 instrument, solutions in deuterated chloroform being used for investigations with this technique, unless otherwise specified.

Mass spectra were obtained by using a Hitachi RMN 6E spectrograph and the ultraviolet absorption spectra were recorded from methanolic solutions by means of a Unicam SP800 spectrophotometer.

RESULTS

SOLUTIONS STORED UNDER NITROGEN

The opened ampoules all exuded a thiol-like odour, suggesting cleavage of the molecule across the C–S link in the 8-1 position.

COMPONENT AT R_F 0·7—

Infrared spectrometry—Peaks (λ_{max}) occurred at the following values: 3210, 1690, 1480 and 1 270 cm^{-1} (cyclic urea, –CO–NH–) and 2 580 cm^{-1} (thiol, –SH), see Fig. 1.

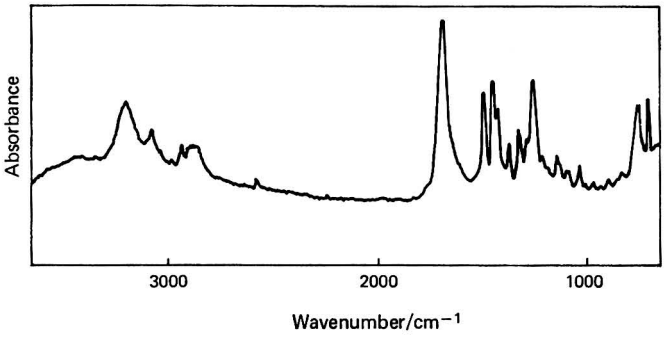


Fig. 1. Infrared spectrum (with a potassium bromide disc) of the component at R_F 0·7

Nuclear magnetic resonance spectrometry—The following were observed: 1 proton (triplet) at τ 8·62 attributed to –SH; 2 protons (A_2 of A_2B_2) at τ 7·42 attributed to the $-CH_2-$ next to –SH; 3 protons (B_2 of A_2B_2 *plus* a triplet) at τ 6·70 attributed to the $-CH_2-$ adjacent to the previous $-CH_2-$, *plus* one proton of a ring methylene group; one proton (triplet) at τ 6·20 attributed to the second proton of a ring methylene group; one proton (broad singlet) at τ 4·00 attributed to –NH; and 5 protons (singlet) at τ 2·67 attributed to a phenyl group, see Fig. 2.

Mass spectrometry—A prominent ion of mass 222 ($C_{11}H_{14}N_2OS$) was obtained. The base peak of the spectrum was at mass 175 ($C_{10}H_{11}N_2O$), further fragmentation due to loss of NHCO producing the prominent ion of mass 132 ($C_9H_{10}N$). A metastable peak at 99·6 confirmed this transition. Further loss of mass 27 (HCN) occurred to produce a prominent ion of mass 105; the transition from mass 132 to 105 is confirmed by a metastable peak at mass 83·5.

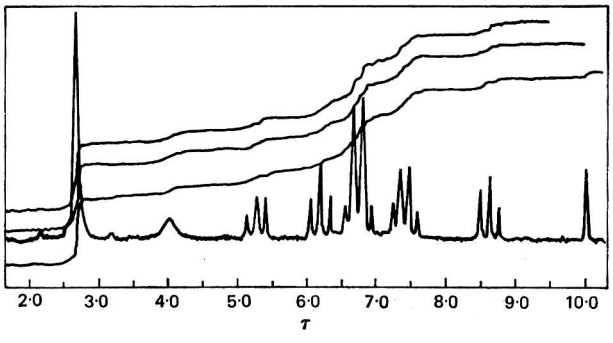
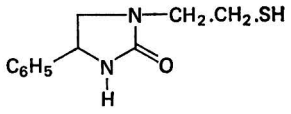


Fig. 2. The 60-MHz nuclear magnetic resonance spectrum of the component at R_F 0·7

From the above observations the suggested structural formula of the component is—



1-(N-β-ethylthiol)-4-phenyl-4,5-dihydro-2-imidazolone

COMPONENT AT R_F 0·3—

Infrared spectrometry—Peaks (λ_{max}) were: 2925 cm^{-1} (NH_3^+), 1660 cm^{-1} (S-alkyl thiocarbamate), carbonyl 1538 cm^{-1} (–NH_3^+ deformation), and 1506, 1582, 1598 cm^{-1} (aromatics, see Fig. 3).

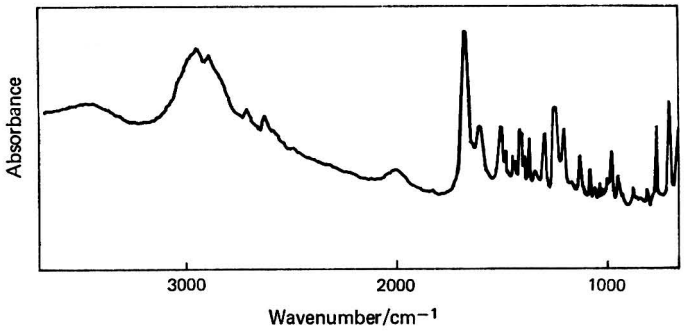


Fig. 3. Infrared spectrum (with a potassium bromide disc) of the component at R_F 0·3

Nuclear magnetic resonance spectrometry—The following were observed: 6 protons *plus* water at τ 6 to 7 attributed to $-CH_2N-CH_2-CH_2-$ and confirmed by the addition of D_2O; 1 proton (triplet) at τ 5·54 attributed to $>CH-NH_2$; 5 protons at τ 2·3 to 2·7 attributed to a phenyl group; and 3 protons at τ 1·0 attributed to $-NH_3^+$ and confirmed by the addition of D_2O, see Figs. 4 and 5.

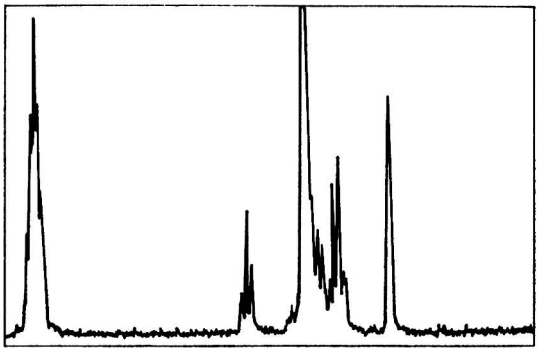


Fig. 5. The 100-MHz nuclear magnetic resonance spectrum of the component at R_F 0·3 after the addition of D_2O

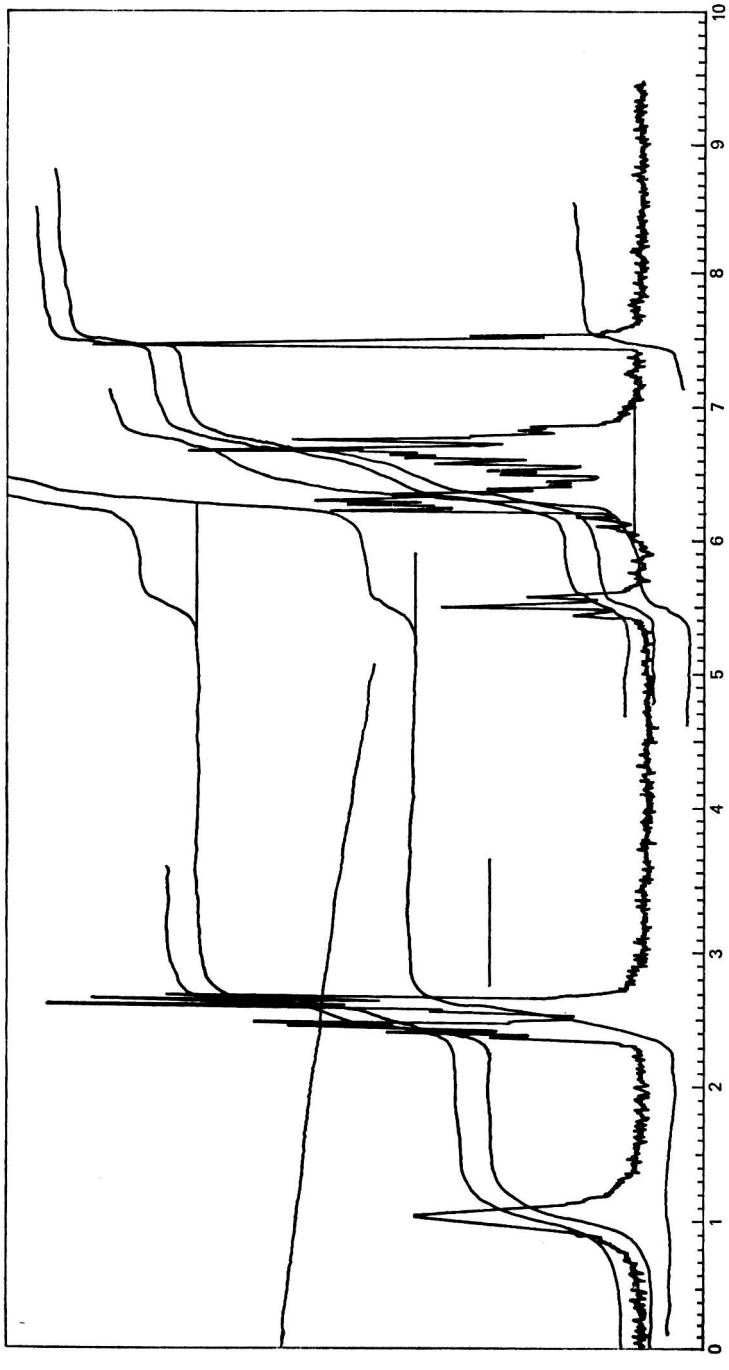
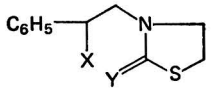


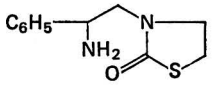
Fig. 4. The 100-MHz nuclear magnetic resonance spectrum of the component at R_F 0·3 in dimethyl sulphoxide

Mass spectrometry—The molecular ion (*m/e* 222) was too weak to measure. There was a pronounced *m/e* 204 corresponding to $(M - H_2O)^+$. This ion is either isomeric with or the same as the molecular ion of the parent compound and the very close resemblance between this spectrum below *m/e* 204 and that of the parent compound suggests that the basic structure is—



Where X and Y are, respectively, –OH and=NH or $-NH_2$ and=O

The molecular weight and the very strong *m/e* 106 (C_7H_8N by measurement) $PhCH{=}NH_2^+$ strongly suggest that the structure is—



3-N-(β-amino-β-phenyl)ethyl-2-thiazolone

This conclusion is supported by the other spectra as described above.

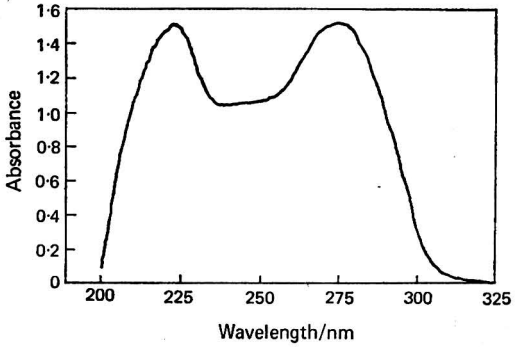


Fig. 6. Ultraviolet spectrum of the component at R_F 0·8

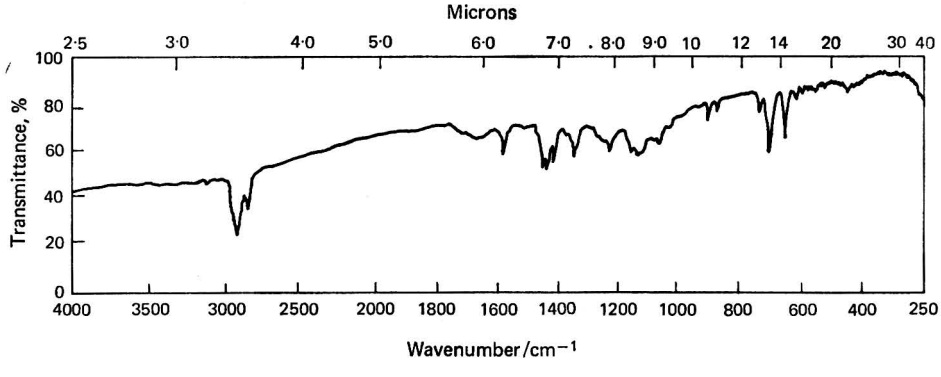
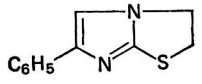


Fig. 7. Infrared spectrum (with a potassium bromide disc) of the component at R_F 0·8

SOLUTIONS STORED UNDER OXYGEN

COMPONENT AT R_F 0·8—

Ultraviolet spectrometry—The wavelengths of the absorption maxima were 275 and 233 nm, and of the minima, 257 and 237 nm, see Fig. 6. The spectrum was identical with that of an authentic sample of 6-phenyl-2,3-dihydroimidazo[2,1-*b*]thiazole—



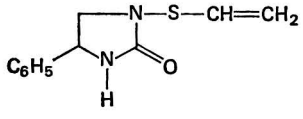
Confirmation was obtained from infrared spectrometry (with the Perkin-Elmer 457) which produced a spectrum identical with that of an authentic sample of the above compound, see Fig. 7.

COMPONENT AT R_F 0·55—

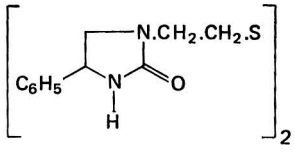
Infrared spectrometry—The peak values (λ_{max}) were 1700, 1490 and 1270 cm^{-1} (cyclic urea), see Fig. 8.

Nuclear magnetic resonance spectrometry—Except for the absence of thiol, the spectrum was virtually unchanged from that obtained for the component at R_F 0·7 present in solutions stored under nitrogen, see Fig. 9 (see p. 242).

Mass spectrometry—This analysis indicated that the molecular ion was at *m/e* 442 with a prominent ion at *m/e* 280—



The spectrum was in accord with the proposed structure—



Bis-[β-(2-oxo-4-phenylimidazolidin-1-yl)ethyl] disulphide

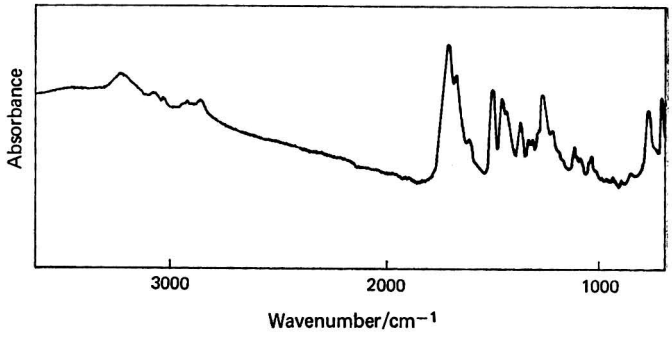


Fig. 8. Infrared spectrum (with a potassium bromide disc) of the component at R_F 0·55

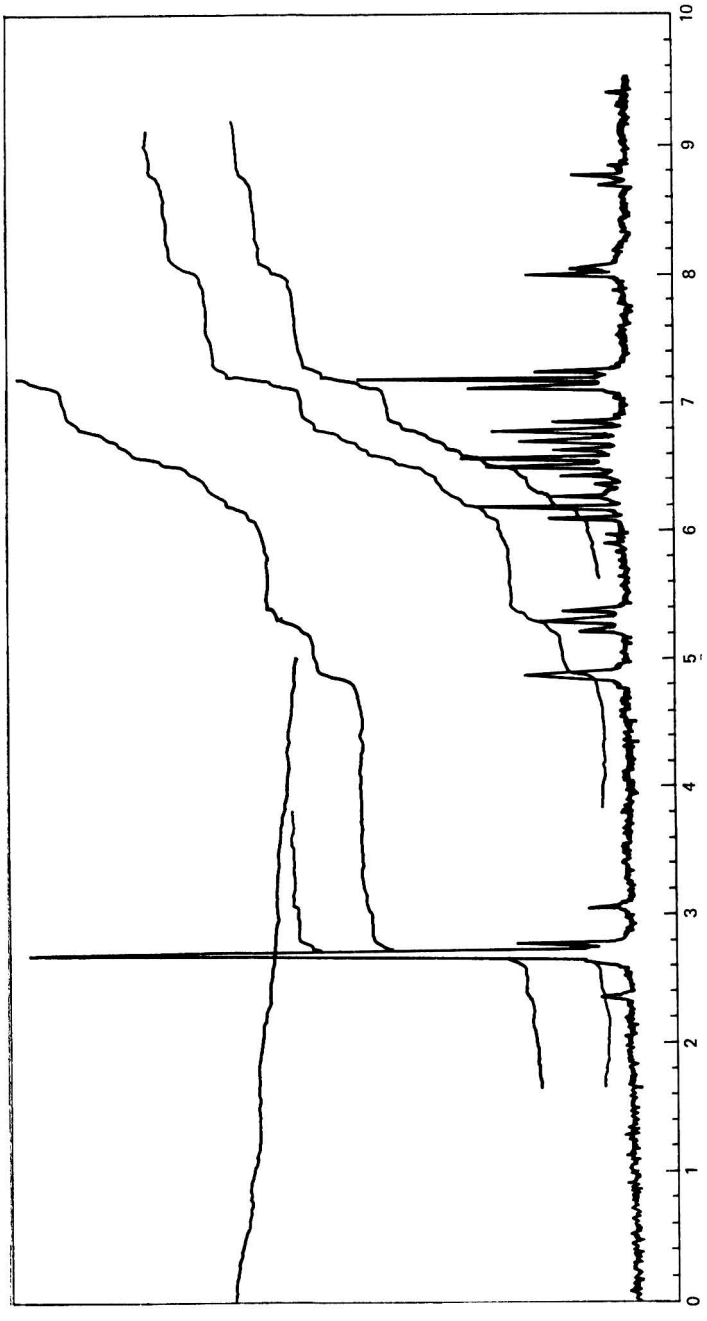
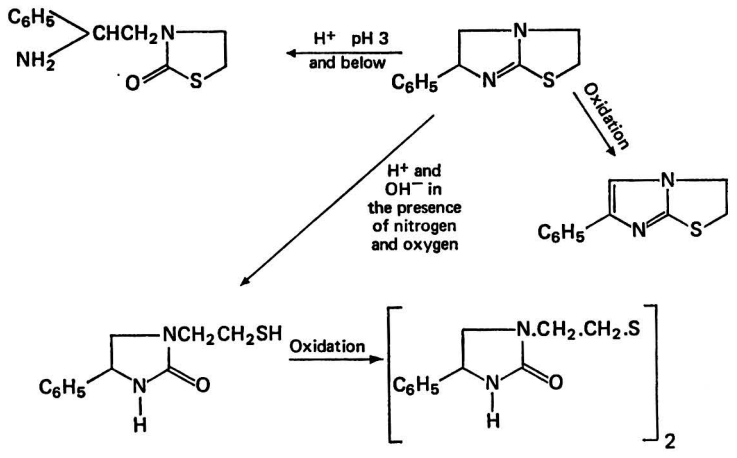


Fig. 9. The 100-MHz nuclear magnetic resonance spectrum of the component at R_F 0·55

From this work it can be concluded that the decomposition mechanism is as follows—



The authors are grateful to Mr. D. J. Greatbanks for obtaining the n.m.r spectra and assisting with the interpretation of the same, to Mr. M. Rix for the mass spectrometry examinations, and to Dr. N. Barton for providing an authentic sample of 6-phenyl-2,3-dihydroimidazo[2,1-*b*]thiazole.

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Levamisole: Its Stability in Aqueous Solutions at Elevated Temperatures

Part II. An Assay Specific for Levamisole and Applicable to Stability Studies

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An assay specific for the anthelmintic drug levamisole is described. The procedure depends on the separation of the active constituent by partition column chromatography in a hexane - water - chloroform - triethanolamine system supported on Celite, followed by ultraviolet spectroscopic measurement of the levamisole in selected fractions of the column eluate.

It has been demonstrated that the laevo isomer (levamisole) is the biologically active moiety of the tetramisole molecule. The method described below will not differentiate between the racemate and the laevo isomer but racemisation of the drug may be monitored by a combination of the chromatographic and a polarimetric assay. The decomposition products of levamisole were reported in Part I (this issue, p. 235) and it is imperative that any method used for stability studies should differentiate between these compounds and levamisole itself.

Tetramisole hydrochloride is readily soluble in water and methanol and has an absorption maximum at 214 nm ($E_1^1 = 860$). However, measurement of the extinction coefficient cannot be used for stability studies because the decomposition products of the drug also absorb at 214 nm. A preliminary solvent extraction of aqueous levamisole solutions, to remove the decomposition products, again does not overcome the problem, nor does the alternative procedure of potentiometric titration because the decomposition product 3-*N*-(β-amino-β-phenyl)ethyl-2-thiazolone has a similar p*k* value and cannot be differentiated. The present work was therefore undertaken with the object of developing an assay specific for levamisole that would be applicable to stability studies.

Experimental

Experience with column partition chromatography suggested a possible means of isolation of the drug for assay purposes. Experiments have demonstrated that levamisole is stable in the partition solvent system used (see Method) and that the procedure described will isolate the parent compound from its decomposition products (see Results). A typical chromatogram for levamisole is shown in Fig. 1.

The absorption of chloroform in the solvent system precluded the measurement of levamisole at its absorption maximum and it was therefore necessary to monitor fractions of eluate at 232 nm, which is on a slope in the spectrum (see Fig. 2). This suggested that the assay might be affected by variations in the degree of partitioning of the chloroform (*e.g.*, due to variation in ambient temperature) or a variation of 1 nm in the wavelength selected on the spectrophotometer. In both instances, however, any error would be removed by assay of the standard at the same time as the sample. Also, with reference to the former possibility, it was found that when the absorption per milligram of the standard was determined periodically at temperatures between 20 and 28 °C for a period of 12 months, the results showed no significant variation and the peak fraction occurred only one fraction earlier at 28 °C.

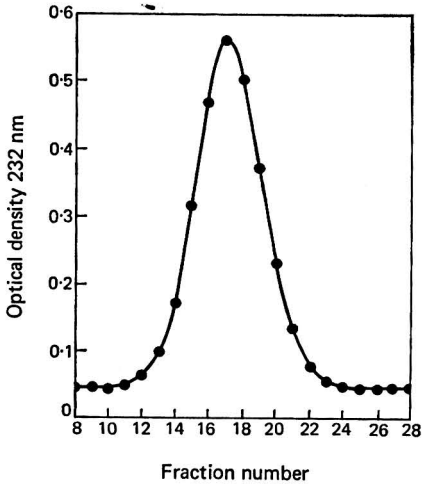

Fig. 1. Chromatogram of levamisole

Consideration was given to omitting chloroform from the system. In practice the drug exhibited an absorption maximum at 209 nm in the eluant phase. This was low and therefore likely to be subject to interference from absorbed impurities that might be present in the solvents or eluted from the Celite.

The procedure may be considered to be unconventional but experience with the assay has shown that it is reliable for the purpose for which it was developed. This point is demonstrated in Part III (this issue, p. 248).

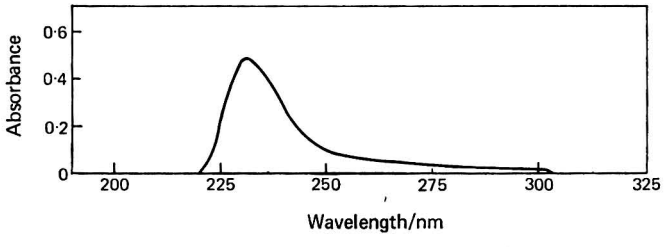

Fig. 2. Ultraviolet spectrum of levamisole dissolved in the eluting agent

Method

Apparatus—

Chromatographic column—A column 700 mm in length and 20 to 23-mm internal diameter, fitted with a sintered disc and tap, is used.

Reagents—

Acid-washed Celite—Transfer 500 g of Celite 545* into a 3-litre beaker and add 2 litres of concentrated hydrochloric acid. Stir the mixture to an even paste and allow it to stand, with occasional stirring, for 12 hours. Decant the bulk of the acid and suspend the residue in 1 litre of water. Filter through a Buchner funnel and wash the residue with water until it is free from acid. Continue the washing with 500 ml of methanol, and finally wash with 1 litre of a mixture of equal parts of analytical-reagent grade methanol and ethyl acetate. Dry the residue at about 100 °C until it is free from solvent odour.

*Made by Johns-Manville Company Ltd., London

Hexane—Hexane of spectroscopic grade is suitable for use without treatment. If this grade is not available, the optical density of the hexane, when read in a 1-cm cell at 254 nm against a 1-cm cell air-blank, must not exceed 0·7. If the optical density reading is greater than 0·7 the hexane must be purified as described below.

Transfer 10 litres of hexane and 100 ml of oleum (20 per cent. of sulphur trioxide) into a suitable container and stir rapidly with a stainless steel stirrer for 30 minutes. Separate the oleum and mix it with an excess of crushed ice. Wash the hexane successively with two 1-litre volumes of water, two 1-litre volumes of 5 per cent. sodium hydrogen carbonate solution and two 5-litre volumes of water. Dry the washed hexane over anhydrous calcium chloride and distil it, collecting the fraction boiling between 65 and 68 °C and checking that the fraction collected complies with the optical density requirements above.

Solvent system—Transfer into a 2-litre separating funnel 850 ml of hexane, 800 ml of methanol (AnalaR), 50 ml of chloroform B.P., 200 ml of water and 20 ml of triethanolamine (Hopkin and Williams GPR). Shake the mixture vigorously for 3 minutes and allow it to stand for 40 minutes before use. The upper layer constitutes the eluting agent and the lower layer the stationary phase.

Preparation of sample—

Because 3-*N*-(β-amino-β-phenyl)ethyl-2-thiazolone has a similar retention time on the chromatographic column to levamisole and absorbs at the same wavelength, it is necessary to convert it to the dithiocarbamate.[1] Transfer a quantity of the sample containing about 40 mg of levamisole to a 50-ml standard flask and dilute to volume with water. Pipette 10 ml into a 50-ml separating funnel, add 3 ml of 5 N sodium hydroxide solution and extract with four 15-ml portions of chloroform B.P. Run the extracts into a 100-ml standard flask, add 10 ml of an ethanol - carbon disulphide (1 + 1) solution and adjust to volume with chloroform, allowing the flask and contents to stand for 10 minutes. Evaporate a 10-ml aliquot to dryness at room temperature in a stream of nitrogen. Add 1 ml of the ethanol - carbon disulphide solution to the residue and evaporate it to dryness as previously described. Then dissolve the residue in 1 ml of stationary phase *plus* 1 drop of ethanol - carbon disulphide, add 2 g of acid-washed Celite, and mix well.

The above procedure is repeated with pure standard levamisole.

Preparation of chromatographic column and subsequent treatment—

Transfer 15 g of acid-washed Celite into a 250-ml beaker and add 7·5 ml of stationary phase with a 10-ml straight-sided pipette. Thoroughly mix the stationary phase with the Celite and pack the mixture into the column, adding the mixture in portions of about 3 g and packing down with a tamper after each addition. Add a weighed amount of the prepared sample mixture. Then open the tap at the bottom of the column and carefully add eluting agent to a depth of about 12 inches above the packing.

Continue the development with eluting agent and collect successive 10-ml volumes of eluate in 6 × 1-inch stoppered tubes. Collect forty fractions and measure the optical density of each in a 1-cm cell on a suitable spectrophotometer at 232 nm (the absorption maximum of levamisole when dissolved in this eluting agent) against a reference of eluting agent. Finally, repeat the above procedure by using the prepared standard mixture in place of the sample. The recommended time for a 10-ml fraction is about 2 minutes.

Calculation of results

Levamisole produces a symmetrical chromatogram (Fig. 1).

$$\text{Percentage w/w of levamisole} = \frac{\Sigma \text{ Optical densities between minima of sample peak} - (\text{residual absorption} \times \text{number of fractions})}{\Sigma \text{ Optical densities between minima of standard peak} - (\text{residual absorption} \times \text{number of fractions}} \times \frac{\text{Weight of standard (mg)}}{\text{Weight of sample (mg)}} \times 100$$

Results

Samples of the decomposition products referred to in the previous paper were mixed individually with known amounts of levamisole and the mixture assayed for levamisole content by the above method. The results are given in Table I.

Table I

Results of assays of mixtures of levamisole and decomposition products

Decomposition product	Theoretical amount of levamisole, per cent. w/w	Levamisole recovered, per cent. w/w
1-(*N*-β-Ethylthiol)-4-phenyl-4,5-dihydro-2-imidazolone ..	60·5	59·3
Bis-[β-(2-oxo-4-phenylimidazolidin-1-yl) ethyl] disulphide..	66·0	65·9
3-*N*-(β-Amino-β-phenyl)ethyl-2-thiazolone	74·4	73·1
6-Phenyl-2,3-dihydroimidazo [2,1-*b*] thiazole	59·0	59·2

The authors wish to acknowledge the expert technical assistance of Miss J. Glass.

Reference

1. Feigl, F., "Spot Tests in Organic Analysis," Sixth Edition, Elsevier, Amsterdam, 1960, p. 270.

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Note—Part I of this series appears on p. 235.

Analyst, March, 1971, Vol. 96, *pp.* 248–253

Levamisole: Its Stability in Aqueous Solutions at Elevated Temperatures

Part III. A Chromatographic and Polarimetric Study of the Kinetics of Degradation

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Levamisole is hydrolysed by both acids and alkalis. At 100 °C decomposition is at a minimum at pH 2, while at pH 8 the rate of decomposition is increased about 70-fold. From kinetic studies at pH 4 and 8 the stability of the drug at 25 and 37 °C has been predicted.

THE decomposition products produced by levamisole in solution have been described by the above authors in Part I of this series (this issue, p. 235). The dehydro compound produced by oxidation of levamisole was determined at pH 8 and found to be less than 1·5 per cent. for almost total decomposition of the parent compound. Hence, in this work, the decomposition of levamisole was treated as being primarily due to hydrolysis.

The present study utilised the chromatographic assay previously described in Part II of this series (this issue, p. 244), together with a polarimetric evaluation to check for racemisation.

EXPERIMENTAL

A typical production batch of levamisole was used throughout this work.

DETERMINATION OF pH PROFILE—

Solutions containing 0·5 per cent. of levamisole were prepared at pH 2·2, 3·0, 4·0, 5·0, 6·0, 7·0 and 7·9 by using double-strength McIllvaine's buffer system and stored under oxygen in an incubator at 100 ± 1 °C as described in Part I. The ampoules were sealed under oxygen instead of air to ensure that the reaction would not slowly terminate because of a shortage of oxygen.[1] Samples were removed at pre-determined time intervals for assay by column chromatography and polarimetry, the latter by Perkin-Elmer 141 polarimeter. The polarimetric assay consisted of measuring the optical rotation of the sample at 589 nm in a 1-dm glass cell jacketed with water which had been equilibrated to room temperature (23 °C).

Then,

$$[\alpha]_{589}^{23} = \frac{\text{observed rotation}}{\text{path length (dm)} \times \text{concentration of solution (g ml}^{-1})} \times 100$$

and percentage of levamisole in solution $= \dfrac{[\alpha]_{589}^{23} \text{ test solution}}{[\alpha]_{589}^{23} \text{ control solution}} \times 100$

where the control solution was of the same composition as the test solution but differed in that it had not been stored at 100 °C. The pH of the solutions was shown to have remained constant throughout the series.

EFFECT OF BUFFER CONCENTRATION ON THE RATE OF DECOMPOSITION AT pH 4—

Some 0·5 per cent. solutions at pH 4 were prepared and stored as described previously, this time including disodium hydrogen phosphate and citric acid at concentrations shown in Table III (see p. 251). For economy of time and effort the polarimetric assay was used, earlier work not reported here having shown that the infinity value for the assay was zero.

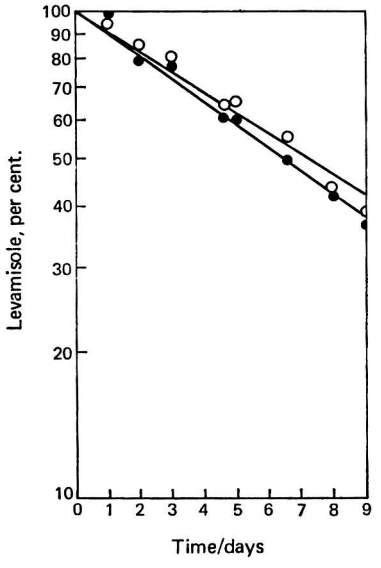

Fig. 1. Decomposition of a 0·5 per cent. solution of levamisole buffered to pH 2·2 and stored at 100 °C under oxygen. ● chromatographic assay, and ○ polarimetric assay

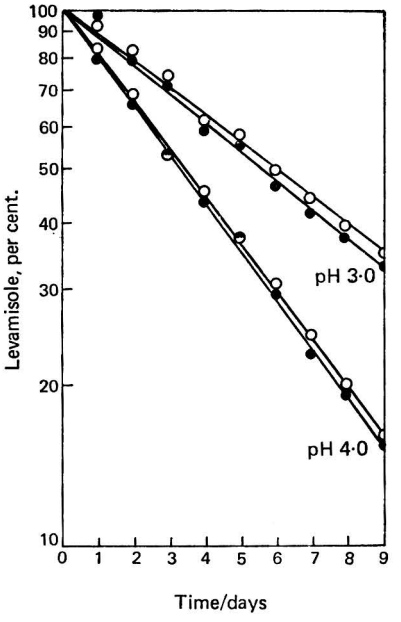

Fig. 2. Decomposition of 0·5 per cent. solutions of levamisole buffered to pH 3·0 and 4·0 and stored at 100 °C under oxygen. ● chromatographic assay, and ○ polarimetric assay

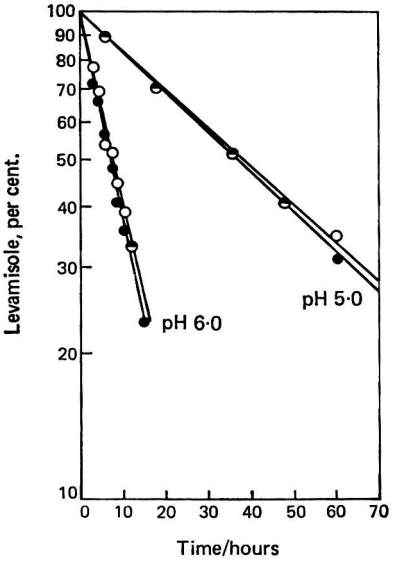

Fig. 3. Decomposition of 0·5 per cent. solutions of levamisole buffered to pH 5·0 and 6·0 and stored at 100 °C under oxygen. ● chromatographic assay, and ○ polarimetric assay

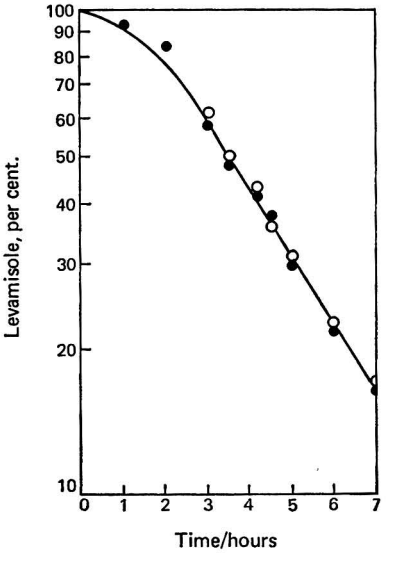

Fig. 4. Decomposition of a 0·5 per cent. solution of levamisole buffered to pH 7·0 and stored at 100 °C under oxygen. ● chromatographic assay, and ○ polarimetric assay

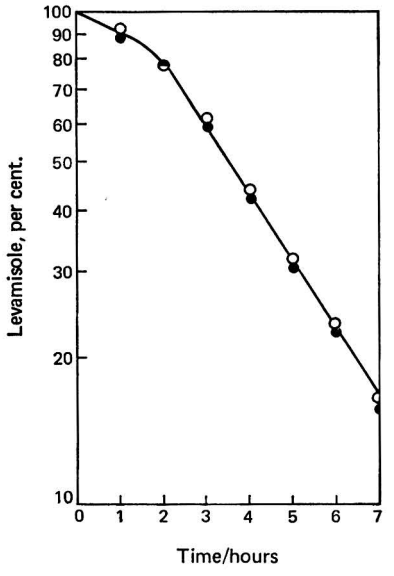

Fig. 5. Decomposition of a 0·5 per cent. solution of levamisole buffered to pH 7·9 and stored at 100 °C under oxygen. ● chromatographic assay, and ○ polarimetric assay

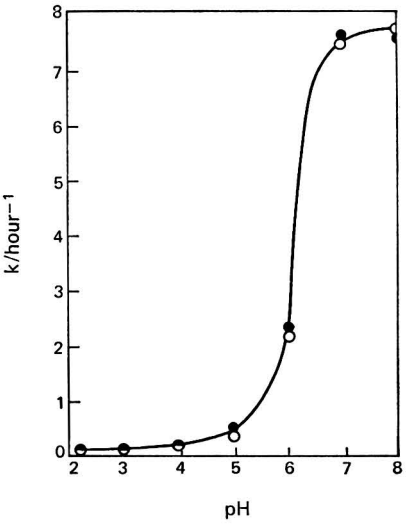

Fig. 6. pH profile for levamisole at 100 °C. ● chromatographic assay, and ○ polarimetric assay

TEMPERATURE DEPENDENCY AT pH 4 AND pH 7·9—

Solutions (0·5 per cent.) at pH 4 and 7·9 were prepared and stored as described previously at 101, 90, 80, 71 °C and 97·2, 82·5, 76·5 and 67·6 °C, respectively. Samples were removed for assay by polarimetry at pre-determined time intervals.

RESULTS AND DISCUSSION

DETERMINATION OF pH PROFILE—

The results are presented graphically, see Figs. 1 to 6. The initial curvature of the regression at pH 7·0 and 7·9 is explained by the rapid rate of fall in potency of the solution compared with the time the solution takes to reach a steady 100 °C. The gradient of the graph was calculated from the linear portion.[2]

The results were statistically analysed by a Telecomp computer and are presented in Table I.

A comparison of the results obtained by the two methods of assay was made as follows—

$$\text{Degrees of freedom} = (n_1 - 2) + (n_2 - 2)$$

where n_1 is the number of determinations done by chromatographic assay and n_2 the number by polarimetric assay.

TABLE I

STATISTICAL ANALYSIS OF RESULTS FOR pH PROFILE

	Chromatographic assay		Polarimetric assay	
pH	Standard error of regression slope	Slope of regression (k)/day^{-1}	Standard error of regression slope	Slope of regression (k)/day^{-1}
2·2	0·005	0·118	0·007	0·115
3·0	0·004	0·129	0·002	0·129
4·0	0·002	0·206	0·001	0·202
5·0	0·007	0·456	0·009	0·428
6·0	0·053	2·290	0·009	2·260
7·0	0·204	7·670	0·231	7·760
7·9	0·158	7·660	0·161	7·550

A significant difference between the chromatographic and polarimetric assays may be investigated by use of Student's t-test—

$$t = \frac{\text{difference between } k_1 \text{ and } k_2}{\sqrt{(\text{standard error } k_1)^2 + (\text{standard error } k_2)^2}}$$

where k_1 is the slope of the regression line derived from the chromatographic assay results, k_2 the slope derived from the polarimetric assay results, and t is dependent on the number of determinations done by each assay method. If it is to have any significance at a 5 per cent. level its value must not be greater than the values given for t_{limit} in Table II.[3]

TABLE II

COMPARISON OF THE RESULTS OBTAINED BY THE CHROMATOGRAPHIC AND POLARIMETRIC ASSAYS

pH	Degrees of freedom	t_{limit}	t, found by experiment
2·2	12	2·18	0·42
3·0	16	2·12	1·74
4·0	16	2·12	1·69
5·0	9	2·26	2·40
6·0	13	2·16	0·18
7·0	10	2·23	1·76
7·9	8	2·31	0·64

The statistical analysis of the results shows that there is no significant difference between the polarimetric and chromatographic assays. This demonstrates that in aqueous solution, over the pH range studied, the drug does not racemise and also that in the interests of economy of time and effort, the polarimetric assay can be used instead of the chromatographic one. At pH 5 the t value is slightly high. However, reference to Fig. 3 shows that the drug has not racemised as the results from the chromatographic assay are slightly lower than those obtained with the polarimetric assay. Because significance at a 5 per cent. level is being considered, one set of results in twenty can be expected to give a high experimental t value.

At constant temperature and pH the decomposition of levamisole is a first-order reaction. This is shown by the linear log concentration *versus* time graphs. The decomposition is acid - base catalysed and optimum stability occurs within the pH range of 2 to 3. The rate of decomposition rapidly increases between pH 5 and 7 and at pH 8 it is about seventy times faster than at pH 2. The small difference between rate constants at pH 7 and 7·9 is consistent with the view that the rate of decomposition varies with the concentration of free base. The pk_a of levamisole at 100 °C is 6·75.

EFFECT OF BUFFER CONCENTRATION ON THE RATE OF DECOMPOSITION AT pH 4—

The results are presented in Table III.

TABLE III

THE RATE OF DECOMPOSITION OF LEVAMISOLE AT pH 4 IN DIFFERENT BUFFER CONCENTRATIONS AT 100 °C

Buffer	Concentration/M			
Phosphate	0·10	0·20	0·30	0·40
Citrate	0·05	0·10	0·15	0·20
Time/days	Levamisole, per cent.			
0	100	100	100	100
1	82·0	81·8	82·1	81·6
2	67·3	67·0	67·5	67·7
3	55·0	56·1	55·2	55·0
4	47·1	46·4	47·8	47·5
5	38·0	39·8	37·3	38·6
pH after 5 days	3·5	3·5	3·7	3·9

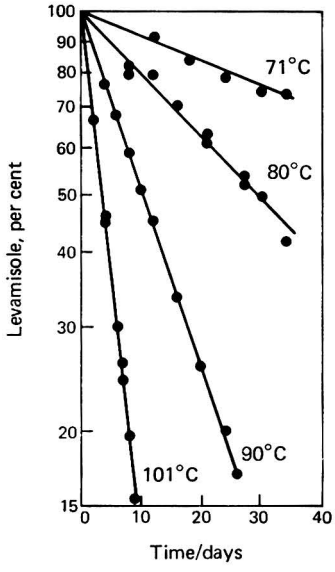

Fig. 7. Graphs showing the stability of levamisole in solution at pH 4·0 when stored at various temperatures

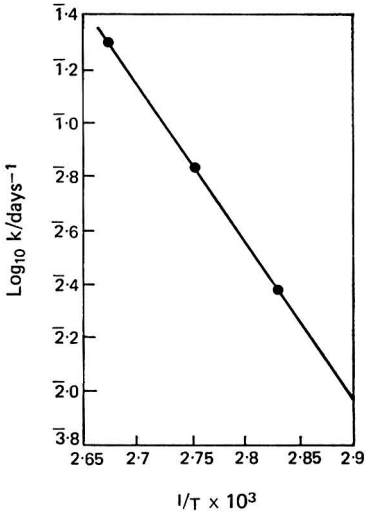

Fig. 8. Effect of temperature on decomposition (Arrhenius' equation) for levamisole insolution at pH 4·0

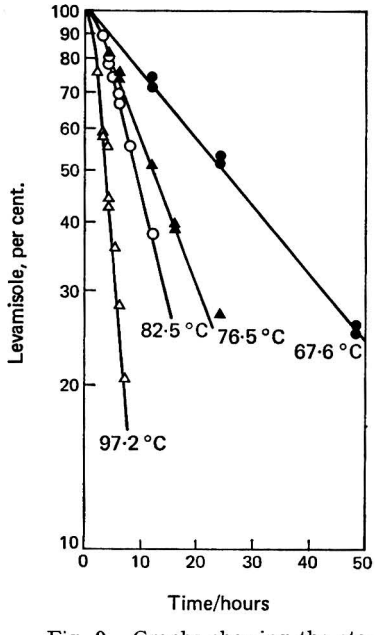

Fig. 9. Graphs showing the stability of levamisole in solution at pH 7·9 when stored at: ●, 67·6 °C; ▲, 76·5 °C; ○, 82·5 °C; and △, 97·2 °C

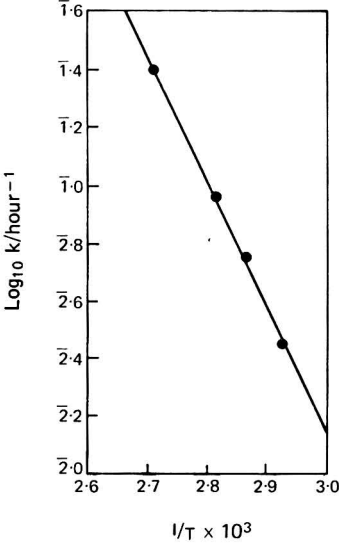

Fig. 10. Effect of temperature on decomposition (Arrhenius' equation) for levamisole in solution buffered to pH 7·9 and stored under oxygen

It is evident that different concentrations of phosphate and citrate ions have no effect on the rate of decomposition of levamisole, and that the rates of decay previously determined over the pH range of 2 to 7·9 were due to variations in solution pH alone and not to catalytic species such as phosphate and citrate ions from the buffer salts. The same evidence shows that the salt effect must be negligible.

The slight fall in pH associated with the 0·1 in phosphate *plus* 0·05 in citrate, 0·2 in phosphate *plus* 0·1 in citrate and 0·3 in phosphate *plus* 0·15 in citrate molar buffer solutions demonstrates their inadequate buffer capacity for studies of the rate of decomposition of levamisole in solution.

TEMPERATURE DEPENDENCE AT pH 4 AND pH 7·9—

The results are graphically presented in Figs. 7 to 10. A programme for a KDF 9 computer to deal with the statistical analysis and prediction of shelf-life as described by Clark and Hudson[1] was used. The salient characteristics of the computer print-out are as follows—

Activation energy at pH 4 = 26·4 kcal mole^{-1}

Activation energy at pH 7·9 = 18·6 kcal mole^{-1}

TABLE IV

PREDICTED POTENCY LOSS OF 0·5 PER CENT. SOLUTIONS AT pH 4·0 AND 7·9 AFTER 2 YEARS' STORAGE AT 25, 30 AND 37 °C

pH	Temperature/ °C	Strength, per cent.	Lower confidence limit (95 per cent.)
4·0	25	98·4	98·2
	30	96·7	96·4
	37	91·3	90·6
7·9	25	0·0	0·0
	30	0·0	0·0
	37	0·0	0·0

The results in Table IV show gross instability of levamisole at pH 7·9, with a significant increase in stability at pH 4·0.

To obtain further information from the kinetic study, the entropy of activation was calculated by substituting the values obtained for the activation energy and rate constants at 100 °C and pH 4 and 8 in the equation described by Laidlaw and Eyring,[4]

$$k = \frac{KT}{h} e^{-\frac{\Delta H\ddagger}{RT} \times \frac{\Delta S\ddagger}{R}}$$

where k is specific reaction rate at 100 °C at the corresponding pH, K is Boltzman's constant, h is Planck's constant, R is the gas constant, T is the temperature in °K, $\Delta H\ddagger$ is the heat of activation and $\Delta S\ddagger$, the entropy of activation.

Also,

$$\Delta H\ddagger = E - RT$$

where E is the activation energy and the other terms have the same notation as above. At pH 4, $\Delta S\ddagger$ is $-18{\cdot}2$ cal mole^{-1} °C^{-1}, and at pH 7·9, $\Delta S\ddagger$ is $-30{\cdot}2$ cal mole^{-1} °C^{-1}.

The figures for the entropy of activation are in agreement with those given in the literature for ester hydrolysis. The higher figure of $-18{\cdot}2$ cal mole^{-1} °C^{-1} at pH 4 may be explained by the fact that the cation attracts water molecules and is solvated to a greater extent than the free base. Conversely, at pH 7·9, the lower entropy figure of $-30{\cdot}2$ cal mole^{-1} °C^{-1} is in keeping with what would be expected for the free base where more arranging of the solvent molecules is necessary before a reaction can occur.

We thank the Management Services Department, I.C.I. Ltd., Pharmaceuticals Division, for assistance with the statistical analysis.

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1. Clark, C. J., and Hudson, H. E., *Manuf. Chem. and Aerosol News*, 1968, **37**, 40.
2. Scott, M. W., and Lachman, L., *J. Pharm. Sci.*, 1962, **51**, 125.
3. Lindgren, B. W., "Statistical Theory," Macmillan Co., New York and London, 1962.
4. Laidlaw, K. J., and Eyring, H., *Ann. N.Y. Acad. Sci.*, 1940, **39**, 303.

NOTE—Parts I and II of this series appear on p. 235 and p. 244, respectively.

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Book Reviews

THE DESTRUCTION OF ORGANIC MATTER. By T. T. GORSUCH. Pp. viii + 151. Oxford, New York, Toronto, Sydney and Braunschweig: Pergamon Press. 1970. Price £2·75; $7.50.

This is an important contribution to the literature of analytical chemistry. The text gives ample support to the statement on the dust cover that ". . . it has been recognised that the severe conditions often employed for the removal of organic matter may easily introduce more error than all the other steps in the procedure combined." So the need for this comprehensive and critical survey becomes self-evident.

A short chapter deals with methods that involve little or no preliminary treatment. Such methods are limited to samples in which the organic matrix or residual organic matter offers no interference with the physical or chemical procedures that are subsequently to be used for the determination of inorganic constituents.

There follows a discussion of sources of error, *e.g.*, contamination from apparatus and losses of trace elements by adsorption. Methods of wet and dry oxidation, oxidative fusion and other procedures are discussed in the next three chapters.

The chapter on methods of investigation is of particular interest. Attention is focused on the use of radiochemical techniques for tracing the channels whereby trace elements may be lost during the process of destroying the organic matter. This is the field in which Dr. Gorsuch has made a unique and valuable contribution in his own researches, and his treatment of the subject provides a concise and lucid introduction to these methods. An appendix provides nuclear data on radioactive tracers.

Wet and dry methods for the destruction of organic matter are next discussed as preliminaries to the determination of metallic and other elements, treated individually, both in their organic compounds and as impurities in organic matter. The text is annotated with a wealth of literature references and it is here that the reader is brought to realise the degree of conflict in the conclusions reached by many workers. Indeed, the author frequently stresses the need for further recovery investigations in many experimental circumstances. Considering the extent of such uncertainties, the diversity in the nature of samples and the variety of oxidation methods available it is only to be expected that guide lines, rather than specific directions, are commonly given. Acceptable explanations are often advanced, as concerns, for example, the differing risks of loss of certain metals as a consequence of the presence of chlorine in the ionic or covalent state.

A final chapter gives details of selected decomposition procedures with guidance on their respective spheres of applicability.

The text is in clear terms, and the book is well produced at a reasonable price, as book prices go in these days. There is, however, a regrettable number of obvious typographical errors that will, no doubt, be corrected in future editions. And the reviewer has no doubt that further editions will be called for.

The many chemists who are concerned with the destruction of organic matter as a step in analytical procedures will be more aware of the pitfalls that await them if they provide themselves with this book. They will also generally be forearmed as well as forewarned.

W. C. JOHNSON

CHEMISTRY AND PHYSICS OF CARBON. Volume 6. Edited by PHILIP L. WALKER, JUN. Pp. xiv + 354. New York: Marcel Dekker Inc. 1970. Price $23.50; £11·20.

Carbon is a unique element for several reasons, not the least of which is the range of properties shown by its elemental forms and the way that systematic study of those properties yields data of theoretical as well as practical value. This monograph series has set a high standard for reviews and articles that place the experimental data in a wider context, and the four chapters of Volume 6 maintain that standard.

Maire and Méring, with an article on "Graphitization of Soft Carbons," relate the adsorption of bromine to the Fermi level in the solid and hence to the level of defects present at various stages of graphitisation. The process is seen as the scavenging of tetrahedral carbon atoms left

behind by the carbonisation stage rather than the mutual orientation of already perfect layer planes, as in the Franklin model. Taylor and Kline in "Effects of Reactor Irradiation on the Dynamic Mechanical Behaviour of Graphites and Carbons" describe how the pattern shown by the temperature variation of internal friction can be used to give detailed information on the amount and nature of radiation-damage processes in graphite.

To readers of *The Analyst*, however, the articles of greatest interest are probably those by Puri on "Surface Complexes on Carbons," and by Avgul and Kiselev on "Physical Adsorption of Gases and Vapors on Graphitized Carbon Blacks." Coincidence though it may be, the presence of these two articles in the same volume enhances its importance to those concerned with the surface properties of carbons.

The article on physical adsorption is a digest of two decades of work in the Moscow school of A. V. Kiselev. Graphitised carbon blacks are chosen as substrates because their relatively homogeneous surfaces give data of value to adsorption theory while also being of practical interest for the increasing use of such absorbents in chromatography. Thermodynamic characteristics of adsorption are calculated from the theory of molecular interactions and molecular statistics with the objective: "the prediction of adsorption properties with an accuracy that will satisfy practical needs." Already, the twenty tables of physicochemical data relating to graphitised carbon blacks and the 270 references to original papers will be of great value.

By contrast, many of the adsorbent carbons used by chemists are valued precisely because their surfaces are not homogeneous but provide active sites for chemisorption. Professor Puri describes the formation, decomposition and reactions of the surface complexes with oxygen, hydrogen, nitrogen, the halogens and sulphur so that one can understand why the behaviour of the carbons depends so much on the history of their formation and treatment. About 300 references add to the value of the review.

This volume is essential reading for any chemist using carbons or graphites who wants to understand the reasons for their behaviour. Its typography, illustrations and binding are uniformly good and no serious errors have been noted. What a pity that the economics of book production should make such a financial sacrifice necessary for individual ownership! JOHN WRIGHT

SOLVENT EXTRACTION OF METALS. By A. K. DE, S. M. KHOPKAR and R. A. CHALMERS. Pp. x + 259. New York, Cincinnati, Toronto, Melbourne and London: Van Nostrand Reinhold Co. 1970. Price £6.

This is a splendid book—a quality product in every respect. It gives an up-to-date survey of solvent-extraction chemistry as applied to the determination of metals, and also indicates the possibilities for the separation of anions and organic species. An amazing amount of data and detail is given in the space of 259 pages, and yet the organisation of the book is such that it is easy to locate information regarding a particular extraction system or a particular metal.

The book begins with a chapter devoted to theoretical considerations of the basic principles involved in solvent extraction procedures (45 pages, mathematical, but not *too* heavy).

Separate chapters are then devoted to the solvent extraction systems based on each of the following nine classes of reagent: β-diketones; 8-hydroxyquinoline and its derivatives; oximes and dioximes; cupferron and analogous compounds; nitrosophenols and pyridylazonaphthol; dithizone; dithiocarbamates, xanthates and dithiol; organophosphorus acids, esters and oxides; high molecular weight amines. The authors do not claim that the literature survey in these chapters is exhaustive, but the reader is certainly given an adequate and up-to-date guide to the literature on each topic, the actual number of references cited varying from 61 on oximes and dioximes to 281 on β-diketones and 315 on organophosphorus acids, esters and oxides.

The penultimate chapter deals with molecular and ion-association compounds. The final chapter, on selective extraction procedures for metals, is particularly useful; it deals separately with the metals of Groups I - VI, with the 3*d*, 4*d* and 5*d*-block metals, lanthanides and actinides. There is a very comprehensive subject index.

In their preface, the authors venture to express the opinion that "solvent extraction is perhaps the most versatile of all analytical techniques." It certainly has an extremely wide range of application, and there is no doubt whatsoever that this reference book for analytical chemists in research and industry merits inclusion on every practical chemist's bookshelf. Furthermore, the cost represents good value for money in terms of current prices. D. M. W. ANDERSON

AN INTRODUCTION TO ^{19}F NMR SPECTROSCOPY. By E. F. MOONEY. Pp. viii + 95. London, New York and Rheine/Westf.: Heyden & Son Ltd., published in co-operation with Sadtler Research Labs. Inc., Philadelphia. 1970. Price £3·75; $9.00; DM 34.00.

Nuclear magnetic resonance spectra of fluorine-19 are more like those of protons than the spectra of many other elements. This is because the ^{19}F nucleus of spin 1/2 is 100 per cent. abundant and has a high magnetogyric ratio and, consequently, high sensitivity. The chief difference is that chemical shifts up to 300 p.p.m. and some large coupling constants may occur. Dr. Mooney is right when he claims that a simple book of examples of fluorine spectra is required. This he has provided and it will be welcomed by many teachers, especially for use with practical interpretation classes associated with summer schools and other short courses. It is correctly described as an introduction and is not suitable as a complete manual, as it does not contain a full table of chemical shifts or make other attempts to be comprehensive.

With over 100 spectra in fewer than 100 pages, there is not much space for text beyond notes on the spectra; these notes are generally helpful and sound. There is no strong thread of continuity through the collection other than that indicated by the chapter headings: Introduction; Fluoroaliphatics; Perfluoroalicyclics; Fluoroaromatics; Fluorinated Heterocyclics; and Inorganic Fluorine Compounds.

The book would be easier to use if more attention had been paid to some details. A re-ordering of spectra could ensure that the full spectra and the enlarged sections were printed alongside each other. The captions could be re-arranged so that they appear on the same page as the figure to which they refer. The use of scales showing both chemical shifts and frequencies on all figures would avoid much multiplying by 56·4 and a fruitless search to confirm that the proton spectra were observed at 60 MHz.

In summary, this book constitutes a useful set of spectra and notes for about eighty compounds.

D. H. WHIFFEN

CATALYST HANDBOOK; WITH SPECIAL REFERENCE TO UNIT PROCESSES IN AMMONIA AND HYDROGEN MANUFACTURE. Pp. viii + 231. London: Wolfe Publishing Ltd. for Imperial Chemical Industries Ltd. 1970. Price £3·15.

Few industrial concerns can claim such extensive use of catalysts on a large scale as I.C.I. Thus the scientists of the Agricultural Division of that company are well suited to producing this interesting and informative book, which is intended to dispel the "mystery" with which industrial catalysts are regarded by many users. The book certainly succeeds in this task. It is somehow reassuring to find that the catalysts for hydrocarbon-reforming reactions (including the naphtha reforming process), for carbon monoxide removal and for ammonia synthesis are composed mainly of nickel, copper (or Fe_3O_4) and Fe_3O_4 *plus* small amounts of other oxides, respectively. The dependance of catalytic efficiency on various parameters, including the presence of catalyst poisons, is described for the three types of reaction. In addition, there is a concise introduction to the catalytic properties of solids, and chapters on the structural engineering of catalysts, catalyst testing, de-sulphurisation of feed-stocks, the handling and use of catalysts and computer programs for converter calculations. Such programs allow, for example, the optimal catalyst conditions to be calculated for achieving the most economical conversion under given reaction conditions. Numerous tables of equilibrium constants and other data are appended, as are examples of calculations based on the processes discussed.

Although the book will be of little direct value to the analyst, it does provide him with valuable information about the nature and functioning of industrial catalysts and should give him a greater understanding of why certain analyses are requested (*e.g.*, traces of sulphur in feed stocks, which might be a catalyst poison).

A. TOWNSHEND

LECTURES AND COURSES

TRENT POLYTECHNIC Nottingham

Department of Chemistry & Biology

Head of Department R. Stock, B.Sc., Ph.D., F.R.I.C.

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Course A – Tuesday June 22nd Wednesday June 23rd.

Course B – Thursday June 24th Friday June 25th.

Course Fee £12 (including lunches & light refreshments).

The Course is organised jointly by the Liquid Chromatography Sub Group of the Gas Chromatography Discussion Group and the Department of Chemistry & Biology, Trent Polytechnic. The course will be accented towards the practical side, so that participants may gain as much experience as possible in operating the various machines, using a variety of detectors and techniques.

Further details and application forms can be obtained from the Head of the Chemistry & Biology Department, Trent Polytechnic, Burton Street, Nottingham. NG1 4BU.

Microdetermination of Mercury in Biological Samples
Part II. An Apparatus for Rapid Automatic Determination of Mercury in Digested Samples

Urine samples that have been cold-digested by potassium permanganate - sulphuric acid mixture overnight are analysed in apparatus consisting of an automatic sample changer, pumps for transferring the sample solution to a purgation tower and adding tin(II) chloride solution, which reduces mercury(II) to metallic mercury, and a spectrophotometer. The mercury vapour is liberated from the solution in the tower by a flow of nitrogen and then taken through the absorption cell in the spectrophotometer where the light absorption at a wavelength of 253·7 nm is continuously recorded. After completion of the purgation, the mercury-free solution is transported back to the original tube in the sample changer by reversing the pumps, and the next analysis is started. The mercury content in the sample is calculated from standard graphs, drawn from results with known amounts of mercury. Sixty digested samples, each containing 1 ml of urine, are analysed in about 2 hours without any manual work or supervision. In each sample about 1 ng of mercury can be detected, but normally the working range for urine samples is 0 to 400 ng ml^{-1} of mercury(II). The analysis can be applied to biological or any other samples that can be digested in a similar manner.

G. LINDSTEDT and I. SKARE

Chemistry Department, National Institute of Occupational Health, Fack, S 104 01 Stockholm 60, Sweden.

Analyst, 1971, **96**, 223–229.

Propylene Carbonate Extraction of Tris(pentan-2,4-dione)iron(III) from Aqueous Solution: Application to the Spectrophotometric Determination of Iron

Orange tris(pentan-2,4-dione)iron(III) is extracted from aqueous solution into propylene carbonate at pH 4·0 to 9·0. Distribution coefficients range from 23·9 to 116, depending on the ionic strength and pH of the aqueous phase. Relative standard deviations of the spectrophotometric methods developed are 1·52 per cent. or less and these methods are applicable to the routine determination of 56 to 391 μg of iron. One of the methods was applied to the determination of iron in wrought aluminium alloy. The importance of using non-toxic solvents in analytical chemistry is emphasised.

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Analyst, 1971, **96**, 230–234.

Levamisole: Its Stability in Aqueous Solutions at Elevated Temperatures
Part I. Isolation and Identification of Decomposition Products Formed in Aqueous Solutions of Levamisole Stored under Nitrogen and Oxygen at 100 °C

Solutions of *l*-tetramisole (levamisole) buffered over a pH range of 2 to 8 were stored under nitrogen and oxygen at 100 °C. The decomposition that occurred was detected by thin-layer chromatography. The decomposition products were isolated and their structures elucidated by standard instrumental procedures.

N. A. DICKINSON

Department of Pharmacy, University of Manchester.

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Pharmaceutical Department, I.C.I. Pharmaceuticals Division, Macclesfield, Cheshire.

Analyst, 1971, **96**, 235–243.

Levamisole: Its Stability in Aqueous Solutions at Elevated Temperatures

Part II. An Assay Specific for Levamisole and Applicable to Stability Studies

An assay specific for the anthelmintic drug levamisole is described. The procedure depends on the separation of the active constituent by partition column chromatography in a hexane - water - chloroform - triethanolamine system supported on Celite, followed by ultraviolet spectroscopic measurement of the levamisole in selected fractions of the column eluate.

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Analyst, 1971, **96**, 244–247.

Levamisole: Its Stability in Aqueous Solutions at Elevated Temperatures

Part III. A Chromatographic and Polarimetric Study of the Kinetics of Degradation

Levamisole is hydrolysed by both acids and alkalis. At 100 °C decomposition is at a minimum at pH 2, while at pH 8 the rate of decomposition is increased about 70-fold. From kinetic studies at pH 4 and 8 the stability of the drug at 25 and 37 °C has been predicted.

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Analyst, 1971, **96**, 248–253.

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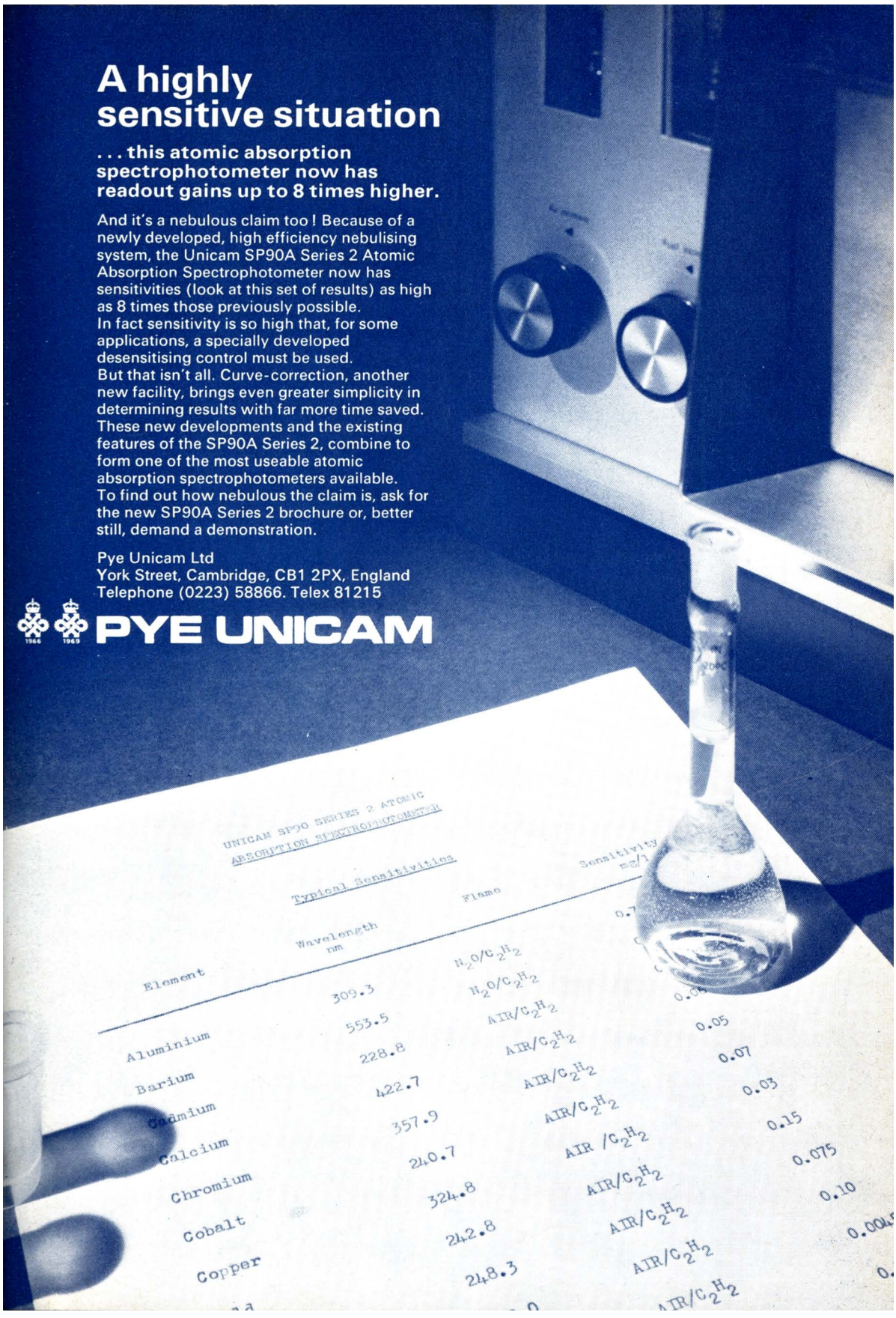

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