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		AIR/C_2H_2	0.02

Summaries of Papers in this Issue

A New Method for the Measurement of Extremely Low Humidities and its Application to the Testing of Desiccants

Measurement of the efficiency of desiccants has in the past been limited in accuracy by the necessity of determining relatively small differences in weight with a lapse of days or weeks between weighings. A method is described, based on the use of the electrolytic hygrometer, whereby this and other difficulties are avoided and an increase in sensitivity of several orders of magnitude is obtained. Results are given for most of the desiccants in common use, and it is shown that some of the more efficient desiccants are capable of drying gases to much lower levels of water content than is suggested by previously published figures.

Appendices describe the more general application of the technique to the determination of water in microgram and sub-microgram amounts from other sources, and also some of the special apparatus used.

J. E. STILL and H. J. CLULEY

The General Electric Company Limited, Central Research Laboratories, Hirst Research Centre, Wembley, Middlesex.

Analyst, 1972, **97**, 1-16.

Assay of Sodium Borohydride by Chloramine-T Oxidation

An elegant and rapid method has been evolved for the assay of sodium borohydride by using chloramine-T as the oxidising agent.

A. R. SHAH, D. K. PADMA and A. R. VASUDEVA MURTHY

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-12, India.

Analyst, 1972, **97**, 17–18.

Determination of Microgram Amounts of Antimony, Bismuth, Lead and Tin in Aluminium, Iron and Nickel-base Alloys by Non-aqueous Atomic-absorption Spectroscopy

Microgram amounts of antimony, tin, lead and bismuth are extracted quantitatively from a 10 per cent. hydrochloric acid solution of the sample containing 2 per cent. of ascorbic acid and 6 per cent. of potassium iodide, in a single 30-s extraction, into a 5 per cent. solution of trioctylphosphine oxide in 4-methylpentan-2-one. The extract is then nebulised directly into the atomic-absorption burner flame.

Use of this technique permits the determination of as little as 0·1 p.p.m. of these metals. The general precision of the proposed method is 5 $\pm$ 0·3 p.p.m.

KEITH E. BURKE

The International Nickel Company Inc., Paul D. Mercia Research Laboratory, Sterling Forest, Suffern, New York 10901, U.S.A.

Analyst, 1972, **97**, 19–28.

The Effect of Various Acids on the Atomic Absorption of Rare Earths

The effects of hydrochloric, sulphuric, nitric and perchloric acids on the atomic absorption of the rare earth elements yttrium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium have been determined. The rare earths can be categorised into two groups according to their behaviour in the four acids. Elements in group I (samarium, europium, dysprosium, holmium, erbium, thulium and ytterbium) showed little change in absorption behaviour in these acids, and no change when the acid concentration was varied from 0·1 to 0·5 M. Yttrium, gadolinium and terbium of group II are sensitive to the type of acid used. Considerable suppression of absorption was caused by sulphuric acid and less severe suppression by nitric acid. The suppression caused by sulphate and nitrate cannot be eliminated with enhancing agents, and these anions should be removed when the above elements are determined. The elements in group II can be determined in 0·1 to 0·5 M hydrochloric or perchloric acid.

Mrs. ARANKA M. SZAPLONCZAY

Bell Canada Northern Electric Research Limited, Ottawa, Canada.

Analyst, 1972, **97**, 29-35.

High Precision Spectrophotometry
Part I. Assessment of the Performance of the Unicam SP3000 Spectrophotometer and its Application to the Determination of Phosphate in Fertilisers and Related Materials

By using conventional, single-beam spectrophotometers the ultimate precision that can be achieved by direct absorbance measurements is about 0·5 per cent. relative. Greater precision can be obtained if measurements are made differentially. Recently, more advanced spectrophotometers have become available that enable measurements to be carried out directly with a precision comparable with that obtained by use of differential techniques. In this paper the performance of such an instrument, the Unicam SP3000, is discussed and its application to the precise determination of phosphate in fertilisers and intermediates is described.

A. C. DOCHERTY, S. G. FARROW and J. M. SKINNER

Imperial Chemical Industries Limited, Agricultural Division, Billingham, Teesside.

Analyst, 1972, **97**, 36–41.

High Precision Spectrophotometry
Part II. The Determination of Ammelide, Ammeline and Melamine in the Thermal Decomposition Products of Urea

An automatic ultraviolet spectrophotometric method is described for the determination of ammelide, ammeline and melamine in the thermal decomposition products of urea; prior separation of the components is unnecessary. A Unicam SP3000 spectrophotometer is used to make absorbance measurements at several different wavelengths and at two pH values. From the absorbance values obtained the concentrations of the amino-*s*-triazines are calculated by using a computer to solve the appropriate simultaneous equations. The constants required in these equations are obtained by calibration of the spectrophotometer with solutions of the pure compounds. A semi-quantitative estimation of triuret is also possible. Interferences caused by biuret and cyanuric acid can normally be ignored, but corrections are required if large amounts are present.

S. G. FARROW, S. R. HILL and J. M. SKINNER

Imperial Chemical Industries Limited, Agricultural Division, Billingham, Teesside.

Analyst, 1972, **97**, 42–51.

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A New Method for the Measurement of Extremely Low Humidities and its Application to the Testing of Desiccants*

BY J. E. STILL AND H. J. CLULEY

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Measurement of the efficiency of desiccants has in the past been limited in accuracy by the necessity of determining relatively small differences in weight with a lapse of days or weeks between weighings. A method is described, based on the use of the electrolytic hygrometer, whereby this and other difficulties are avoided and an increase in sensitivity of several orders of magnitude is obtained. Results are given for most of the desiccants in common use, and it is shown that some of the more efficient desiccants are capable of drying gases to much lower levels of water content than is suggested by previously published figures.

Appendices describe the more general application of the technique to the determination of water in microgram and sub-microgram amounts from other sources, and also some of the special apparatus used.

As long ago as 1842 Dumas[1] mentioned as being well known the fact that calcium chloride would not dry a gas as completely as would sulphuric acid. The testing of desiccant materials has therefore been going on for more than 120 years. During this period the most painstaking and reliable work has been that of E. W. Morley, who published his results on sulphuric acid and phosphorus pentoxide in three classic papers in 1885, 1887 and 1904.[2,3,4] He finally stated that "no gravimetric work which the scientific world has in hand at present would need to take account of the moisture which phosphorus pentoxide leaves in a gas." As the present paper will attempt to show, 66 years later this conclusion still holds.

In quantitative terms, Morley's method (for an account of which his original papers should be consulted) enabled him to determine as little as 0·01 p.p.m. of water by volume, and no subsequent measurements have even purported to reach this degree of sensitivity. Comparisons of a number of desiccants have been made on at least two occasions, by Bower in 1944[5] and by Trusell and Diehl in 1963.[6] The method used on both of these occasions was to pass a stream of moist gas through the desiccant to be tested and then through a so-called "perfect" desiccant; the increase in weight of the "perfect" desiccant represented the weight of water escaping from the desiccant tested. The agreement between the two lists, especially for the better desiccants, is extremely poor and the discrepancies are not in any way systematic.

Bower, of the U.S. National Bureau of Standards,[5] used phosphorus pentoxide as his "perfect" desiccant and found positive results for the water escaping from fifteen other desiccants. He stated clearly that in his experiments true equilibrium was probably not attained but that he was specifically concerned to compare the efficiencies of desiccants under the common conditions of use for drying gases.

Trusell and Diehl[6] published results on twenty-one desiccants in 1963; they used a liquid nitrogen trap as their "perfect" desiccant. Their figures are remarkable chiefly in that not only did they claim a positive result for the water escaping from phosphorus pentoxide, more than 300 times larger than Morley had considered possible, but also they found four other desiccants to be superior to phosphorus pentoxide.

The only method available for this work until fairly recently was the gravimetric method, and when the published figures are examined in detail it is obvious that this has been stretched

* Presented in part at the Second SAC Conference, 1968, Nottingham.

to its limit. Weight differences of a few milligrams (sometimes even less than 1 mg) have to be determined on a four-place balance, with intervals of several days between weighings. Nor would the use of a microbalance help significantly as the size of the absorption tubes would need to be reduced, with a corresponding reduction in the gas flow that could be handled. Another source of error in the gravimetric method is the need to disconnect the trap or absorption tube for weighing as, in addition to the possibility of atmospheric moisture entering through the joint, some part of the dry interior surface at the entry end must be exposed to moist air during the first weighing; the water absorbed by this surface is then swept by dry gas into the tube or trap and replaced by a fresh quantity of water at the second weighing.

From these considerations the need can be seen for a means of measurement which is more sensitive than the gravimetric method, and which can be applied without any disconnection of the apparatus from the gas-flow system. The method described, based on the electrolytic hygrometer, fulfils these requirements.

Experimental

The version of the electrolytic hygrometer developed in these laboratories, some applications of which have already been described,[7] is an instrument almost ideally suited to the testing of desiccants. Its absolute limit of detection is about 0·01 μg of water compared with the 0·1 mg of the balance. In addition to this four-order improvement in sensitivity the hygrometer has the important advantage that it does not need to be disconnected from the gas stream in order to make a measurement; further, a wait of many days between measurements does not affect its accuracy. In the special case of measurements on phosphorus pentoxide there is the further point that allowance does not have to be made for the volatility of this desiccant, which, although very low, was corrected for by Morley[4] in his work.

One of our principal uses for this instrument has been in the measurement of the extremely small amounts of water present in the internal atmosphere of small electrical devices such as transistors. A major difficulty in such measurements is that, because of the tenacious manner in which traces of water are adsorbed by nearly all surfaces, such a device must have the water swept out of it by a volume of dry gas many thousands of times greater than the volume of gas originally present in the device. Unless this dry gas is many thousands of times drier than the gas originally in the device, such a measurement is, of course, meaningless. In this context, therefore, our main interest in desiccants is in the ultimate dryness that each one is capable of producing and in the elapsed time before such ultimate dryness is attained.

For the assessment of moderate desiccants, such as calcium chloride, the electrolytic hygrometer can be used directly, *i.e.*, a current of moist gas can be passed through a tube of desiccant and the hygrometer cell in series. A direct reading that can be recorded if necessary is obtained, the attainment of equilibrium can be checked visually and the effects of variables can be examined quickly.

For the better desiccants there can be no question of using the instrument in this way, as Trusell and Diehl[6] attempted to do without success. The detector cell cannot be expected to be as good an absorber of water as phosphorus pentoxide because, according to Keidel,[8] the actual compound present in the dried coating on the electrodes is metaphosphoric acid, HPO_3. We have tested this aspect experimentally and we find that, considered as a desiccant, a cell in average condition is rather better than the partly hydrated magnesium perchlorate sold as a desiccant for organic microanalysis; it dries a gas containing 1·5 p.p.m. of water to about 0·02 p.p.m., and its zero reading on a rigorously dried gas is 0·05 to 0·1 p.p.m. It can therefore be used for direct measurements down to about 1 p.p.m. without serious error.

The new method that we use at lower levels consists in collecting the very small amount of water passing through the desiccant over a period of hours, days or weeks in a cold trap, then releasing it as a single discrete quantity into the hygrometer cell within a few minutes. This gives a large concentration factor, the magnitude of which depends on the time of collection, so that the detection limit of concentration depends on how long one is prepared to spend on a measurement. Morley,[3] in a more leisurely age, was content to state: "With a current of three litres an hour, the effect measured was not over a decimilligram in two months. To obtain some such quantity as ten milligrams might therefore require ten years." In our own times, perhaps a ten-day collection period might be considered more reasonable.

For such a length of test, and for a gas flow of 100 ml min^{-1}, the detection limit of the hygrometer corresponds to a volume concentration of almost exactly 1 part in 10^{11}, or 0·01 ml of water vapour in 1000 m^3 of gas.

APPARATUS—

The arrangement of the apparatus is very simple. Dry argon (containing 0·02 to 0·05 p.p.m. of water) from a bench supply is passed in succession through a tube filled with a suitable hydrate to act as a source of water, the tube filled with the desiccant to be tested, the cold trap, the hygrometer cell and a Rotameter flow gauge. The gas flow used in these experiments was 100 ml min^{-1}. The output from the hygrometer cell is connected to a recorder and integrator so that the total signal from the cell can be observed when the water collected in the cold trap is released for measurement.

The source of water needs a little consideration; if it produces too little water, a poor desiccant may not have any drying effect, if too much, a good desiccant may become exhausted before reaching its maximum efficiency in terms of the lowest attainable water content in the effluent gas from the desiccant tube. Three hydrates that have been found useful in this work are aluminium ammonium sulphate, $Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$, producing about 1000 p.p.m. of water and useful in testing the poorest desiccants; nickel sulphate, $NiSO_4.7H_2O$, producing about 80 p.p.m. of water and suitable for desiccants of moderate efficiency; and sodium citrate, $NaOOCCH_2C(OH)(COONa)CH_2COONa.2H_2O$, producing about 1·5 p.p.m. of water and used for testing the best desiccants. A small amount of sodium citrate (*e.g.*, as much as will fit in a tube of the same dimensions as the cold traps described below) will last for many months and will allow even a small tube (see below) of an excellent desiccant to reach maximum efficiency before a significant proportion of the desiccant is exhausted.

The desiccant tube used was made of Pyrex glass, 9 mm i.d., the filled portion being 16 cm long. In the single case of phosphorus pentoxide distributed on glass helices this size of tube proved to be inadequate and the ultimate efficiency was not reached; for a final test on this desiccant a larger tube, about 20 mm × 30 cm, was used. The Granusic form of phosphorus pentoxide reached its ultimate efficiency in the smaller tube.

A copper block heater surrounded the filled part of the desiccant tube and this block could be heated to any temperature required for those desiccants that were regenerated *in situ*. During this operation the hydrate tube was not used, dry argon was passed through the system, and the hygrometer served to indicate the completion of regeneration.

For all the better desiccants (those which reached less than 0·1 p.p.m. of water in the effluent gas) the desiccant tube was sealed directly to the cold trap to obviate the possibility of water entering through a joint between them.

TRAPPING—

To take advantage of the high sensitivity available, a trap is needed that will dry the gas to an even lower level than 1 part in 10^{11}. Theoretically, a cold trap at the temperature of liquid oxygen more than fulfils this condition; it should reduce the vapour pressure of water to the equivalent of about 5 parts in 10^{16}. In practice, when such a trap was first tested experimentally the results were extremely disappointing. Two traps (coils of empty stainless-steel tubing immersed in liquid oxygen) were connected in series and moist gas was passed through them. It was found that up to 14 per cent. of the water entering the first trap was collected in the second trap. Numerous such experiments proved that no significant improvement was obtained by altering the material, length or diameter of the coiled tubing or by changing to a bulb type of trap as used by Trusell and Diehl.[6] Not only is a considerable proportion of the water entering lost by such a trap, but a major part of the loss is always found to occur when refilling with liquid oxygen the Dewar flask which surrounds the trap. Several hundred parts per million of water have been found to emerge from such a trap under these circumstances, even though the level of liquid oxygen has not been lower than one-third of the depth of the coil.

Fortunately, when such a trap is filled with a suitable packing material its efficiency is increased by many orders of magnitude. For a gas flow of 100 ml min^{-1}, the rate used in all of this work, a trap consisting of 75 cm of 6-mm bore borosilicate glass tubing is adequate. The middle 50 cm of the tube is bent into a double loop or coil so that it will conveniently fit into a quart-sized Dewar flask and the coiled part is filled with 2·5-mm glass helices confined between short plugs of silica-wool.

There are probably several reasons for the considerable losses observed from empty traps. A high efficiency can not be obtained with such a trap, even when undisturbed, until sufficient ice has collected to transform it into what is, in effect, a partly-packed trap, which would seem to indicate that part of the water can be carried straight through the middle of the tube by laminar flow. The large losses that suddenly occur on refilling the Dewar flask may well be caused by the fracture of ice crystals into tiny fragments, which are then borne out of the cold section by the gas stream; such fracture may be caused by turbulence of the gas or by thermal shock. Whatever the reasons our experimental work has shown that an empty cold trap is far less efficient at atmospheric pressure than it is under vacuum conditions, when the mean free path is greater than, or at least comparable with, the diameter of the trap.

In a final experiment to determine the efficiency of the trap to be used in testing desiccants, two packed traps, as described above, were made in one piece from a 150-cm length of glass tubing, to avoid the necessity for a joint between them. After passing dry argon through both traps at room temperature for 22 days, both traps were cooled in liquid oxygen, and argon containing 80 p.p.m. of water was passed through them for 14 days. The amount of water collected in the second trap was then measured; it was at the limit of detection and was estimated to be equivalent to less than 0·000 02 p.p.m. Because gas that has passed through a good desiccant contains water not at 80 p.p.m. but at a small fraction of 1 p.p.m., it seems reasonable to suppose that in a desiccant test there would be no significant loss from a single trap over a collection period of any reasonable length. Unfortunately, it was not possible to continue the test for a further period because the entry end of the first trap was by then becoming blocked with ice; it was later realised that for an unexceptionable test a lower level of water should be used in the input gas and the test should be continued for several weeks longer.

MEASUREMENT—

For the measurement of relatively large amounts of water (of the order of 1 mg or more) the electrolytic hygrometer does not require calibration; the weight of water corresponding to a given area on the recorder chart or to a given number of integrator units can be calculated from Faraday's law. At lower levels the peak area from a known amount of water is always less than expected, and the relative discrepancy increases as the amount decreases. Typical factors for the three upper ranges of the instrument were given in an earlier paper.[7] It is therefore necessary, in the measurement of very small amounts of water, to calibrate each peak by producing a peak of roughly the same area from a known amount of water.

The method of calibration described in our earlier paper[7] for use on the higher ranges of the instrument consisted in carrying into the cell a small amount of water evolved from the decomposition of a known weight of a hydrate such as hydrated barium chloride. This method cannot be used on low ranges because the weight required would be too small and the blanks impossibly large.

We have therefore adopted a coulometric method for calibration, the apparatus for which is described in Appendix II. A very small flow of hydrogen is produced by electrolysis and oxidised to water in a stream of otherwise dry argon. The rate of flow of hydrogen is known from the electrolysis current and for work with desiccants it is usually set to produce 5 or 10 p.p.m. of water in the argon. By means of a special valve this moist gas of known composition can be diverted for a known period through the hygrometer cell that is to be calibrated. A concentration of 5 p.p.m., switched through the cell for just under 2 s, produces the 0·01 μg that represents the limit of detection. For calibration of the larger peaks that are produced by most desiccant tests the "moist" gas supply is passed through the cell for several seconds or minutes, whichever is necessary in order to reproduce the area of the test peak as closely as possible. The amount of water represented by the calibration peak being known, that from the desiccant test is calculated by simple proportion from the two area measurements or integrator readings.

In some of the tests on desiccants a calibration valve of the type described was connected between the cold trap and the cell; in others the cell was removed for calibration after conclusion of the test.

The usefulness of this method is by no means confined to the testing of desiccants and its application to the measurement of microgram and sub-microgram amounts of water in general is described in Appendix I.

Results

When this work was started the results obtained were in general agreement with those of other experimenters since the time of Morley, that is to say, all the best desiccants, including an efficient liquid oxygen trap, appeared to give results between 0·1 and 2 p.p.m. As the method has been gradually refined, introducing one precaution after another over more than four years, it has become apparent that not only are the better desiccants much more efficient than at first appeared, but also that there are much bigger differences between them than earlier work had suggested.

Table I shows the results obtained for a number of desiccants, for the hygrometer cell and for a liquid oxygen trap. The results for the same desiccants obtained by Bower[5] and by Trusell and Diehl[6] are included when available and these have been converted to parts per million by volume so as to be directly comparable.

Table I

Efficiencies of some common desiccants, expressed as p.p.m. of water vapour by volume in the gas leaving the desiccant

Desiccant	Results obtained by Bower, 1944	Trusell and Diehl, 1963	Present authors
Calcium chloride	480	135	90 to 160 (according to temperature)
Silica gel	8	95	40 (laboratory stock from oven at 110 °C)
Silica gel	—	—	0·2 (dried *in situ* at 350 °C)
Magnesium perchlorate (hydrated)	40 ($3\ H_2O$)	2·0 ($1{\cdot}5\ H_2O$)	0·10 ($1{\cdot}5\ H_2O$)
Molecular sieve 5A ..	—	—	0·06 (dried *in situ* at 350 °C)
Hygrometer cell	—	—	0·02 (at 1·5 p.p.m. input)
Magnesium perchlorate (anhydrous)	2·7	0·3	0·000 08 (dried *in situ*)
Alumina	1·4	3·9	0·025 (dried, from stock bottle)
Alumina	—	—	<0·000 01 (dried *in situ* at 250 °C)
Phosphorus pentoxide (distributed powder)	0 (standard)	4·8	<0·000 01
Phosphorus pentoxide (Granusic)	—	—	<0·000 01
Liquid oxygen (or liquid nitrogen) trap	—	0 (standard)	<0·000 01

Discussion

If previously published values obtained by a number of experimenters over many years are to be amended by factors of up to 10^4, it is necessary not only to be confident that the new results are correct but also to give sound reasons as to why the earlier results are believed to be in error.

A detailed consideration of the experiment leading to a single result in the present series demonstrates the most important of these reasons. This relates to the lengthy periods that must elapse before the gas leaving the desiccant reaches its lowest attainable water content; the long time scale is presumably caused by the very slow equilibration rates occurring at the extremely low water concentrations involved.

Fig. 1 shows the progress of an experiment on anhydrous magnesium perchlorate that lasted for nearly three months. The horizontal lines show the lengths of the collection periods for the successive tests and their ordinates indicate the average water content of the exit gas during each period. The graph drawn through the mid-points of these lines shows the concentration of water entering the cold trap in parts per thousand million. It can be seen that 5 days elapsed before the concentration was down to ten times the final figure and that it took 1 month to reach twice the final figure. It is perhaps worth noting that the other tests on "ultimate" desiccants followed a similar course; *e.g.*, an experiment on phosphorus pentoxide ran for 6 months, and after 55 days, including several test periods, the water concentration over a 22-day test period was still 0·000 05 p.p.m. From the shape of the graph in Fig. 1 it can be deduced that if a state of equilibrium had been assumed to have been reached within 12 or even 24 hours of the start the result would have been in the p.p.m. range rather than thousandths of 1 p.p.m. Trusell and Diehl's equilibration time, before their first weighing, was a maximum of $\frac{3}{4}$ hour; Bower, as noted earlier, was aware that in his experiments true equilibrium was probably not reached. Similar considerations apply to other, more restricted, work described in the literature, *e.g.*, that of Guérin and Girard.[9]

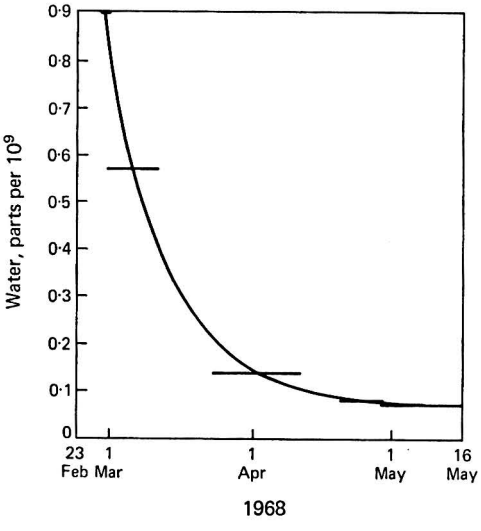

Fig. 1. Progress of a typical desiccant test

Another dubious feature of Trusell and Diehl's method was their use of unlubricated spherical ground-glass joints "as customary in gravimetric gas absorption work." The use of such joints is reasonable when the work is, for instance, an organic carbon and hydrogen determination in which the utmost dryness attained during the experiment is probably not better than 5 to 10 p.p.m. To prove whether or not such joints could properly be used for work on desiccants we tested one that was sealed directly to a cold trap, rigorously dried argon being passed through the joint and trap in series. We found that when clean and dry the joint let in 2·3 to 2·5 p.p.m. of water continuously over 4 days. Very light greasing of the ground surfaces (without forming a continuous film) reduced the diffusion of water through the joint to one tenth of its previous value (0·24 p.p.m.). Thus it would appear that differences in the quality and condition of such joints could also account for Trusell and Diehl's results.

In the light of all the difficulties that have been experienced the results given can hardly be considered to be final, but because each successive refinement of the method has always led to lower, rather than higher, results it seems unlikely that the true values could be higher than those given. As to the true figure for phosphorus pentoxide, it still seems reasonable to repeat Morley's words of 66 years ago, already quoted in the first paragraph. Any actual

determination will have to await the development of an even more sensitive method, and it is likely that even if such a method becomes available the time necessary to reach an ultimate figure will prevent the result from being of more than academic interest.

We have reached certain conclusions as to the applicability of the various common desiccants to our own work or similar work carried out by other investigators.

The two best "ultimate" desiccants are phosphorus pentoxide and the liquid oxygen (or liquid nitrogen) trap as described. We have not been able to distinguish between them on the basis of performance; the cold trap has the obvious disadvantage that it needs refilling twice in every 24 hours unless some automatic device is available for this purpose. It should perhaps be mentioned that the reason for the use of liquid oxygen rather than liquid nitrogen was simply that there was available for other purposes a constant supply of very dry argon which it was decided to use for this work, and argon would be condensed by liquid nitrogen.

Phosphorus pentoxide has been used in two forms, as powder distributed on 2·5-mm or 4-mm glass helices (according to the size of drying tube), and in the granular form that has recently been marketed under the name of Granusic. The latter seems to be preferable in that a smaller bulk of it is needed to give the same ultimate dryness and its actual capacity for water is much greater than that of an equal bulk of distributed powder.

Anhydrous magnesium perchlorate is only slightly inferior to phosphorus pentoxide and it has a very high moisture capacity, but because to attain this high efficiency it needs to be prepared *in situ* by the careful dehydration of the partially hydrated salt, its use is not worthwhile except perhaps in special circumstances.

The partially hydrated magnesium perchlorate commonly sold (often under the name Anhydrone) as a desiccant for organic microanalysis is excellent for such purposes but is useless as an "ultimate" desiccant, being at least three orders of magnitude inferior to phosphorus pentoxide.

The efficiency of silica gel depends very much, as the table shows, on its pre-treatment. It is worth noting that the colour change of the self-indicating variety from blue to pink occurs only at water concentrations well above 1000 p.p.m.; at or below this level it will remain blue indefinitely. Silica gel is therefore useless as an indicator to show the exhaustion of a preceding non-indicating desiccant unless the gas entering is known to contain at least several thousand p.p.m. of water.

Alumina and molecular sieves are both very useful as pre-driers to take the bulk of the water out of a wet gas prior to the use of one of the "ultimate" desiccants; their particular value is in their ease of regeneration by heating in an oven. Alumina can be brought into the class of "ultimate" desiccants if it is regenerated in the tube in which it is to be used by heating to 250 °C in a current of very dry gas.

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Appendix I

Method for measuring discrete microgram amounts of water

The general method to be described lends itself to the measurement of any small amount of water than can be released over a reasonably short time (preferably not more than 4 to 6 hours) into a stream of otherwise dry argon or nitrogen. By taking all the precautions described, amounts as small as a few tenths of a microgram can be measured to an accuracy of about ±20 per cent.; one such measurement can take 5 days or more, most of which is waiting time. Amounts in the microgram range require fewer precautions and less time, while the accuracy can improve to ±5 per cent. or better.

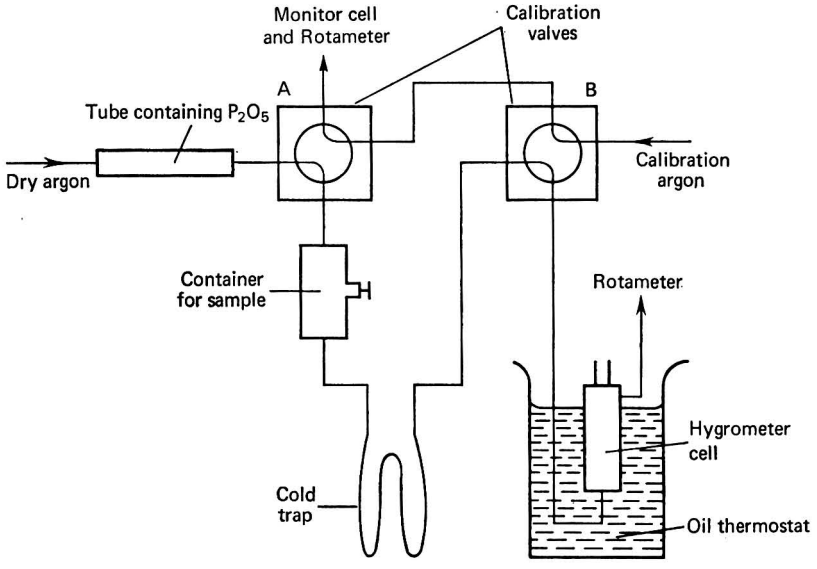

Fig. 2. Arrangement of apparatus for determining very small amounts of water

APPARATUS—

This is described in order of gas flow and is shown diagrammatically in Fig. 2.

Dry argon supply—The extreme dryness required is best appreciated with the help of an example. Consider a small device of volume 1 cm^3, the gas in which contains 100 p.p.m. of water vapour (many electrical devices nowadays are smaller and the gas drier than this). The volume of water vapour to be measured is then 0·1 μl. It will require from 2 to 4 hours to sweep this volume of water quantitatively into a trap with dry argon, so that the volume of argon required at 100 ml min^{-1} will be 12 to 24 litres. If the blank from 20 litres of argon is to be less than 20 per cent. of the amount to be measured, the water content of the argon must be less than 0·001 p.p.m.

A bench supply of dry argon cannot usually be maintained with less than 0·02 p.p.m. of water, even if all tap glands and glass-to-metal joints have solid PTFE inserts, therefore an additional phosphorus pentoxide drying tube is required; this should be about 20 mm in diameter and 30 cm long and should have a Kovar glass-to-metal seal at its exit end. Such a seal is preferable to a thin copper Housekeeper seal because the latter type is sometimes very slightly permeable to water.

Calibration valve A—This is one of the double two-way valves described in Appendix II. Its use is in the introduction of small, known increments of water that exactly simulate water from the source to be measured so that the efficiency of trapping and measurement can be checked and a cell factor (Note 1) determined. The calibration flow of argon is usually maintained at 10 p.p.m. of water for this type of measurement.

Because of the use of PTFE as the rotating member, this type of valve is not completely impermeable to water and prolonged tests have shown that when used in the open laboratory it can let about 0·012 p.p.m. of water into an otherwise dry gas flow of 100 ml min^{-1}. The working parts of valve A are therefore enclosed in a polythene bag (made from lay-flat tube), sealed to the valve body with O-rings surrounding the ports and flushed continually with dry argon (also at about 100 ml min^{-1}). Under these conditions the gas leaving the polythene envelope contains 50 to 100 p.p.m. of water and this degree of dryness in the atmosphere surrounding the valve reduces the water penetration to about 0·0005 p.p.m., which is just acceptable (but see Note 2, below).

Source of water—This is usually in the form of a brass or stainless-steel container fitting fairly closely to the outside of the device to be tested, having a gas inlet and outlet and some

form of pin or plunger that can be used to pierce or crush the device at the appropriate time. The main essentials in its design are that any necessary seals or glands should be of PTFE and should be as small as possible, so as to reduce water permeability to the minimum.

Cold trap—This should be of glass, in the form already described. The joints at its ends should be either glass-to-metal seals with pipe couplings brazed to the metal, or glass sockets with brass cones waxed into place. (Apiezon W wax has been found best for this purpose; greased joints are unsatisfactory, while picein requires too high a temperature and is brittle, so that a joint made with it may separate because of differential contraction on cooling.) A stainless-steel trap packed with stainless-steel gauze has been tried, but was found to release retained water on heating even more slowly than the glass trap.

To release the water from the trap, a Dewar flask containing distilled water at 70 to 80 °C is substituted for that containing liquid oxygen. The temperature of the water should remain roughly constant during the ½ hour or more required to clear the trap and it should also be about the same from one occasion to the next. To this end a small coil of bare Nichrome wire, dissipating 10 to 12 W from an adjustable low-voltage a.c. supply, is suspended near the bottom of the Dewar flask; neither stirring nor thermostatic control is necessary. A suitable slotted cover of thin aluminium sheet is provided for either flask when in position on the trap and a plain cover for when it is not in use. These covers serve to minimise cooling and evaporation of the hot water and accumulation of ice in the liquid oxygen.

Calibration valve B—This is used to introduce small amounts of water directly into the measuring cell to calibrate the response of the cell and to compare the efficiency of such direct measurement with that of measurement of a similar amount released after being held in the cold trap. Its use is also necessary to moisten the cell slightly after very dry gas has passed through it for a long time to raise the reading to a level that is reasonable for setting the zero of the integrator. Any trace of water that may enter through this valve does not accumulate in the trap, it merely raises the zero reading of the cell very slightly. As this has no effect on the measurement, valve B need not be provided with a dry gas envelope.

Measuring cell—It is preferable to immerse the cell, entry end down, in a small oil thermostat with the oil up to the level of the gas exit. The thermostat is best kept at about 40 °C; the response of the cell is then more rapid than at room temperature, while the heat is not sufficient to damage the cell. If the temperature of the cell is not controlled changes in the laboratory temperature cause a drift of the zero reading, and because such changes are usually in an upward direction during the daytime, this drift can make the integration of peaks very difficult (Note 3).

Flow gauge—This is used to verify that the flow of argon through the system is approximately 100 ml min^{-1}. Small variations from this figure do not affect the accuracy of measurements, but the test flow and the calibration flow should be approximately the same and the two paths from a calibration valve to the atmosphere should have about the same resistance at the time when the valve is operated. If, for instance, a Rotameter flow gauge is connected to the calibration monitor but not to the exit from the measuring cell, on operation of a calibration valve there will be a surge of gas from the calibration line caused by the reduction of pressure at the valve, and a falsely large amount of water will be injected into the trap or the measuring cell. The reverse will apply if the gas path through the measuring cell has a higher resistance to flow than that through the calibration monitor. Some further notes on connections and joints are given the last paragraph of Appendix II.

Recorder and integrator—Measurement of such water contents as these will usually be made on the 10-p.p.m. range of the hygrometer and even on this range the peaks may be very small. It is best to use a recorder whose range can be changed from 10 mV to 1 mV. Such a recorder can be adjusted by the control on the hygrometer box to read correctly on the 10-mV range; if it is then switched to the 1-mV range it will show a full-scale deflection for 1 p.p.m. of water and should give measurable peaks down to about 0·01 μg of water.

A mechanical or electromechanical integrator operated from the recorder is not likely to be satisfactory for this work because of mechanical friction and the discontinuous stepping action of the recorder slide-wire, both of which become more serious at low levels.

A very satisfactory electronic digital integrator has been made by some simple additions to a Solartron digital voltmeter; these additions are described in Appendix III. If such an instrument is not available, and more especially if the detector cell is to be used without a thermostat for measuring very small peaks, the best method is to record the peaks on the

1-mV full-scale range and then to cut out the peaks and weigh the chart paper or to use a planimeter. These methods, although more troublesome to carry out, have the advantage that it is possible to decide on the best base-line for each peak after the whole series of peaks has been recorded.

METHOD

Enclose the device whose water content is to be measured in its container ready for breaking or piercing. Connect the container to the calibration valve A and allow dry argon to flow through it for 1 to 2 hours before connecting its exit to the cold trap. Place the hot-water Dewar flask so that the trap is immersed and leave the dry argon flowing until the water content indicated by the measuring cell has reached a suitably low level. This will be about 0·2 p.p.m. or less, and if sufficiently low it will not be affected by exchanging the hot water for liquid oxygen for a few minutes. The drying process will take at least 3 to 4 days and probably longer. It can be monitored by cooling the trap in liquid oxygen overnight and measuring the peak produced by heating it the next morning. Typical figures for such successive overnight blanks, starting the first one 7 to 8 hours after assembling the sample container, would be 3, 1, 0·5, 0·25 and 0·15 μg. The last figure would correspond to about 0·01 $\mu g\ h^{-1}$, which is a satisfactory level. (Note 4.)

When conditions are seen to be satisfactory the integrator zero can be set (Note 5), with the trap still in hot water. Then, substitute liquid oxygen for the hot water, and when the trap has completely cooled, break or pierce the device in its container. Keep the liquid oxygen on the trap for as long as is judged necessary (usually 2 to 4 hours) (Note 6), then put back the hot water and record and integrate the peak.

From calibrations that have been carried out with calibration valve B during the drying period, estimate as closely as possible that period at a water concentration of 10 p.p.m. which will give a peak of about the same area. Return the liquid oxygen to the trap, operate calibration valve A for the required period (keeping the trap cold for the same length of time as was used for the sample), then heat the trap and record and integrate as before. (Note 7.) If the blank is thought to be significant by comparison with the sample and calibration peaks determine it in the same way and subtract its magnitude from those of the other peaks.

Calculate the amount of water taken to obtain the calibration peak and thence by simple proportion the amount released from the sample device.

NOTES—

1. *Cell factor*—This is the factor by which the number of integrator units registered for a particular amount of water must be multiplied to give the theoretical number of units calculated from Faraday's law. For a 0·3-μg amount, as mentioned in note 5, the factor will probably be 3 to 4, rising to 6 or more for 0·1 μg or less and falling to 2 or lower for amounts over 1 μg.

2. *Drying the sample and its container*—A further development of the method will be the mounting of the sample container and calibration valve A inside a glove-box whose nitrogen atmosphere contains about 5 p.p.m. of water. The necessity for separately enclosing valve A will thus be eliminated, and a major advantage will be the ability to introduce a fresh sample device (already dried in the glove-box) without exposure of any surface to moist air. This should greatly reduce the time necessary for drying the system after introduction of each new sample once the apparatus has been initially purged.

3. *Drying the cell*—An electrolytic hygrometer cell coated as described,[7] although fit for use on the higher ranges after drying for 1 to 3 days, does not then reach its minimum reading or become suitable for use in the work now described. The reading on dry gas does not usually fall as low as 0·2 p.p.m. for nearly a month; thereafter, if it has dry gas passing through it for most of the time, its zero reading will decrease further during at least the next 2 months.

4. *Time for passage of water through the system*—A striking demonstration of the retention of small amounts of water on surfaces is given if about 1 μg of water is passed through the sample container and trap from valve A while the trap is hot and after the system is thoroughly dry. In spite of the fact that the total volume between the calibration valve and cell is probably less than 20 ml and that the gas flow is 100 ml min^{-1}, it is likely to take 20 to 30 minutes for the first trace of water to reach the cell. Even then the peak produced will be very low and will last for several hours, yielding an integrated total probably only a small fraction of that produced by passing 1 μg of water straight into the cell. The peak produced in a normal experiment by applying hot water to the previously cooled trap is, of course, much more satisfactory because the whole of the surface that then holds any appreciable amount of water is being heated. It might be argued that the prolonged drying of the sample container could be shortened by heating this also, but unless it could be kept at the

same temperature during the whole determination there would be a risk that the intensive drying would render the container walls liable to retain some of the water from the sample. It is at present thought that the advantages to be gained by putting the sample container and calibration valve in a glove-box, as mentioned above, will be greater than those of heating the container, and the provision of a constant-temperature heated enclosure inside a dry glove-box, though possible, is envisaged only as a last resort if the absolute maximum of sensitivity (and therefore the shortest possible collection time and lowest possible blank) is ever required.

5. *Setting the integrator zero*—Theoretically this should be the level to which the hygrometer reading falls when dry gas has been passed through the system until all traces of water have been stripped from the sample container and the cold trap. In practice, as has been seen, this would take several days, and after an amount of water had passed through the system several days would again be required before the integrator would stop counting. A compromise is therefore necessary; the integrator zero must be set slightly above the true zero level so that each peak is completed in a shorter time. Our usual procedure is to pass 10 p.p.m. of water through the cell from valve B until the hygrometer shows about 2 p.p.m., then to switch back to dry gas and allow the reading to fall for about 1 hour, and at that time to set the integrator zero. Amounts of water are then passed in from valve B, say for 30 s at 10 p.p.m. (about 0·3 μg); if these each take from 20 to 30 minutes to integrate the zero is acceptable. A normal level is from 0·06 to 0·1 p.p.m. above the lowest reading obtained with dry gas.

6. *Time for collection in trap*—The collection time necessary for a particular type of sample and container can be determined by experiment if necessary by using calibration valve A. Too short a time will not allow sufficiently complete transfer of water into the trap; too long a time will mean that the blank will become unnecessarily large in proportion to the water from the sample. Some compensation for these possible errors is provided by the fact that the calibration is carried out, as nearly as possible, under the same conditions.

7. *Recovery of water from trap*—This again can only be a compromise; in general, a given amount of water passed into the trap from valve A and recovered after a suitable period by heating the trap will give a smaller peak than the same amount admitted directly to the cell from valve B, provided that due account is taken of the blank. This phenomenon is partly caused by retention of water beyond any reasonable integration time and partly by the necessary compromise reported above on the integrator zero; a higher proportion is lost from a long low peak than from a high sharp peak of the same theoretical area.

Applications—

The application of the method to the testing of desiccants has already been described. It can also be used for accurate measurements on any very dry gas supply whose water content is too low to be measured directly on the hygrometer scale. A trapping period of from 1 to 20 or 30 hours is normally sufficient to give a peak that is quite easy to measure and to reproduce by calibration. The 100-p.p.m. range of the hygrometer can often be used for such measurements and the method can be simplified by the omission of both calibration valve A and the thermostat for the measuring cell.

It must always be remembered that the time necessary to reach equilibrium in such determinations depends very much on the level of water content being measured. Instances of this have already been given for extreme drynesses of 0·0001 p.p.m. of water and below, but at much higher levels the time required can still be surprisingly long so that another actual example should perhaps be given. The dryness of the bench argon supply was to be measured; for this purpose a cold trap, calibration valve and cell were connected through a 4-foot length of clean $\frac{1}{16}$-inch bore copper tube to a tap on the bench, and 100 ml min^{-1} of argon was passed through the system for 11 days. Four tests were made during the first 5 days with collection periods of 17 to 23 hours each, starting the first test $6\frac{1}{2}$ hours after setting up the apparatus. The results were 0·20, 0·051, 0·028 and 0·019 p.p.m. After a further 6 days, and with a 43-hour collecting period, a result of 0·016 p.p.m. was obtained. It was thus at least 5 days before a fairly close approximation to the true figure was obtained. All these measurements were made on the 100-p.p.m. range of the instrument, calibrating with suitably short periods (20 s to 2·5 minutes) of flow from the calibration line, which was set to give 100 p.p.m. of water.

Another use for the method, or for a suitable modification of it, is for the accurate measurement of amounts of water produced by reactions taking place in dry hydrogen or oxygen. Both these gases give high and not very reproducible zero readings on the electrolytic hygrometer, therefore there is always some uncertainty about measurements made in them, and the difficulty, although lessened, is not completely overcome by the use of a rhodium or gold-plated element in the cell. If the water produced (*e.g.*, by the reduction of an oxide in hydrogen or by the combustion of a hydrogen compound in oxygen) is collected in a cold

trap and later swept out of the trap by a stream of nitrogen or argon for measurement, two advantages are obtained. In the first place the base-line from which the peaks are measured is lower and more reproducible and secondly, the peaks formed by the release of water from a trap are often sharper and more reproducible than those measured directly from a reduction or oxidation reaction as it takes place.

It is not advisable, of course, to change from hydrogen or oxygen to argon and *vice versa* by disconnecting tubing on the apparatus, but one of the calibration valves described is ideal for this purpose. In this system both gases are kept flowing continuously and operation of the valve interchanges them without any risk of the entry of extraneous water. Because measurements in these circumstances are usually made on one of the higher ranges of the instrument the 0·01 p.p.m. or so of water that enters through such a valve is not likely to be significant.

Appendix II

Electrolytic water generator

The essential parts of this apparatus are as follows: an electrolytic cell in which small amounts of hydrogen (and oxygen) are generated; a current supply for the cell; a means of drying the stream of gas that has passed through the electrolytic cell; a heated tube of copper oxide to oxidise the hydrogen; and suitable valves for delivering the calibration gas to various points in the laboratory.

Electrolytic cell—

This is a small glass chamber containing two platinum electrodes sealed through the walls or inserted through small rubber bungs, and having a sintered-glass disc at the bottom through which a stream of argon (or nitrogen) enters.

There is no necessity to place the anode and cathode in separate compartments because the amounts of gas evolved are very small and are swept very rapidly out of the cell; we have not seen any evidence of re-combination of the gases. It is essential for the whole of the contents to be thoroughly stirred by the stream of bubbles entering through the sinter and for the electrodes to be positioned well within the rising stream of bubbles. Unless the electrodes are thoroughly and continuously swept, gas bubbles will cling to them, and at low levels a very small, discrete bubble of hydrogen can cause a noticeable fluctuation in the water content of the calibration gas. The total volume of the cell should not be large; 30 to 40 ml is sufficient, of which 5 to 15 ml is occupied by electrolyte (a suitable electrolyte being formed by 1 to 2 drops of orthophosphoric acid added to distilled water). A small opening, closed by a rubber bung, should be provided near the top for replenishment every 1 to 2 days with distilled water.

Any hydrogen that may be present in the argon or nitrogen supplied to the electrolytic cell will appear as a corresponding amount of extra water in the calibration gas, so that unless the hydrogen content is known to be negligible the gas should be passed through hot copper oxide before use.

Current supply—

The best source of supply is a control box, as used for the electrolytic hygrometer, because it has a voltage-stabilised d.c. output and a meter with appropriate shunts so that its scale is graduated directly in p.p.m. of water. The only addition required is a suitable variable resistance placed in series between the output and the electrolytic cell.

The useful range is from 5 to 2000 p.p.m.; this requires a resistance range of from about 1800 Ω to just over 1 MΩ, which can easily be made up from two or three small radio-type potentiometers and some fixed resistors, with appropriate switching. Some additional accuracy can be gained if necessary by the inclusion of a more accurate meter in the circuit, which will enable the current to be adjusted exactly to the required value of 13·2 μA per p.p.m. of water.

Drier—

This can consist either of two cold traps in series or of a molecular-sieve drier. The former alternative has a smaller volume and allows a more rapid attainment of equilibrium when the output level is changed. It has the disadvantage of requiring refilling of the cold

traps twice a day. The molecular-sieve drier is slower to reach equilibrium but if this is of no particular importance it has the advantage of being less troublesome to maintain.

If cold traps are used the first one should be made with a cylindrical bulb on the entry limb, extending above the level of the liquid oxygen, because a narrow tube would be quickly blocked with ice at this point. The bottom of this limb should be provided with a small drain tube with a polythene cap, so that the ice can be periodically melted and removed. The second loop of the trap should be kept cold by a smaller Dewar flask during this operation so that no appreciable amount of water ever enters the second trap.

A molecular-sieve drier for this purpose can conveniently be a large U-tube with limbs about 2·5 cm in diameter and 45 cm long, having B24 sockets at its ends with the cones secured by Apiezon W wax. A layer of indicating silica gel 1 to 2 cm in thickness, placed about 15 cm from the exit end, will act as a warning that the drier needs to be refilled; it lasts for about 2 weeks at a flow-rate of 100 ml min^{-1} for 24 hours a day.

OXIDISING TUBE—

The tube containing the copper oxide is conveniently made of silica, and the heated part need not be more than about 8 mm in diameter and 10 cm long. A small furnace can be used to heat the tube, or if this is not available a Nichrome wire winding can be applied directly to the silica tube, secured with stainless-steel clips over a layer of asbestos paper, insulated with asbestos string and covered with aluminium foil.

We have found the best filling to be short lengths of fine copper wire (possibly cut from copper braid), which is tightly packed in the tube, heated in oxygen, reduced in hydrogen and then re-oxidised by heating for several hours in oxygen before use. The correct voltage is best found by warming gradually with the winding supplied from a variable transformer, after the rest of the apparatus is assembled, until the correct response is obtained; a temperature of at least 600 °C seems to be necessary. Oxidising agents such as Hopcalite, that act at lower temperatures, have been tried but found to be useless because of retention of water.

VALVES—

For some purposes, such as the checking of hygrometer cells, the apparatus can be connected directly, but for calibration involving the delivery of small, discrete amounts of water a double change-over valve with quick action and minimum dead-space is necessary. We could not find a suitable commercial article at the time at which it was required, so valves were specially made for the purpose to the design shown in Fig. 3. Each valve has two entry points, one each for the test flow and the calibration flow, and two exits, one to the measuring cell (or trap and cell) being calibrated and the other to a monitor cell that serves to check the water content of the calibration line. Normally the calibration stream

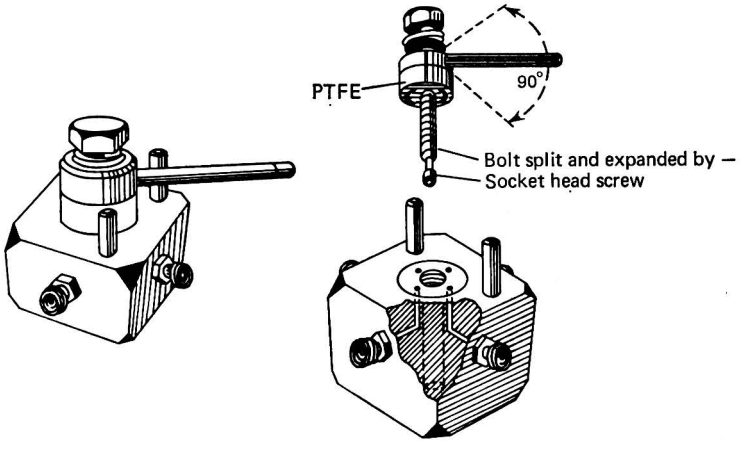

Fig. 3. Calibration valve

is connected to this monitor cell while the dry argon (which will carry the small amount of water to be measured) passes to the measuring cell. Movement of the valve handle through 90° instantly interchanges the connections and allows the calibration stream to flow to the measuring cell for a measured time; the handle is then returned so that the dry argon sweeps the known amount of water into the measuring cell.

A four-port valve, which appears from illustrations to have possibilities for this application, has recently been advertised by the Hamilton Co. of Whittier, California.

It may be convenient to have a number of these valves at different points in the laboratory so that the same water generator can be used for calibration on several experiments. The calibration gas passes from one valve to another in series and is thus available at any point as required (except, of course, that it cannot be used at two valves at the same time). The monitor cell for the calibration stream is attached to the last valve in the line.

There is one reservation to be made as to the use of a number of calibration valves in series. When a particular valve is to be used for a few seconds only, it is necessary for both its exits to have approximately the same resistance to gas flow, as explained in Appendix I. If the particular valve is near the beginning of a long line it is therefore advisable to disconnect the following one while the valve is operated and for a few minutes beforehand. This is all the more necessary if a molecular-sieve drier is used because such a drier has a much larger volume than two cold traps and therefore gives a greater surge of gas when its pressure is lowered.

Joints between the glass and silica parts of the apparatus can be made with waxed (not greased) cone and socket joints, or with metal couplings with PTFE olive-shaped inserts to give compression joints. The remainder of the system is connected by narrow-bore copper tubing having brazed-on brass nipples coupled to brass bodies without O-rings, as used on the hygrometer cell. Stainless steel has been recommended as being slightly easier to dry out than copper, but we prefer copper for its flexibility, cheapness and ease of working. All copper and brass used in such apparatus must have any traces of brazing flux removed, preferably by drilling out followed by prolonged hot-water washing; it must also be thoroughly cleaned with acid internally, then rinsed with water and acetone. Even then the equilibration of a long calibration line at a low water content such as 10 p.p.m. is likely to take many hours, while a system of piping used to distribute dry gas will not attain its lowest possible water content for at least 3 months after assembly.

Appendix III

Integrating attachment for a Solartron LM 1420.2 digital voltmeter

Principle of operation—

The Solartron digital voltmeter is basically a voltage-to-frequency converter followed by a counter. The converter produces a train of pulses at a rate that is linearly proportional to the input voltage, while the counter totals the number of pulses produced during a given time interval. By a choice of suitable parameters, *i.e.*, pulse frequency and count period, the displayed total is made equal to the value of the input voltage. The count period is determined by a clock in the instrument. If the clock is switched off and the counter started manually it will display the accumulated total of pulses generated by the voltage-to-frequency converter. This state is achieved simply on this model of voltmeter by setting the timer slide switch on the rear panel of the instrument to Count. The Auto/Manual switch is set to Manual, and the remaining controls are set to the Volts mode of operation. Thus the digital voltmeter, which is designed to operate either as a voltmeter or as a counter, has now been set to an intermediate mode.

Additional equipment—

Two additions to the voltmeter are required.

Overload counter—The voltmeter counter reads only up to 2999. The output from the hundreds digit is therefore taken from the rear multi-way plug and fed to an electromagnetic counter via a transistor amplifier. The circuit for this is shown in Fig. 4 (*a*); the amplifier draws its power from a supply in the voltmeter.

Set zero control—For zero input voltage to the voltmeter the voltage-to-frequency converter generates 200 pulses s^{-1}. A backing-off circuit is therefore introduced between the input to the voltmeter and the voltage to be measured. This circuit consists of a Mallory cell and coarse and fine potentiometers, as shown in Fig. 4 (*b*). These controls are also used to set the zero of the integrator to the zero reading of the hygrometer or of any other instrument with which it is to be used. All voltages below this set zero level are represented by zero pulses per second and therefore do not contribute to the total count.

Both the above circuits, with the counter, can conveniently be mounted in a single, small, die-cast box.

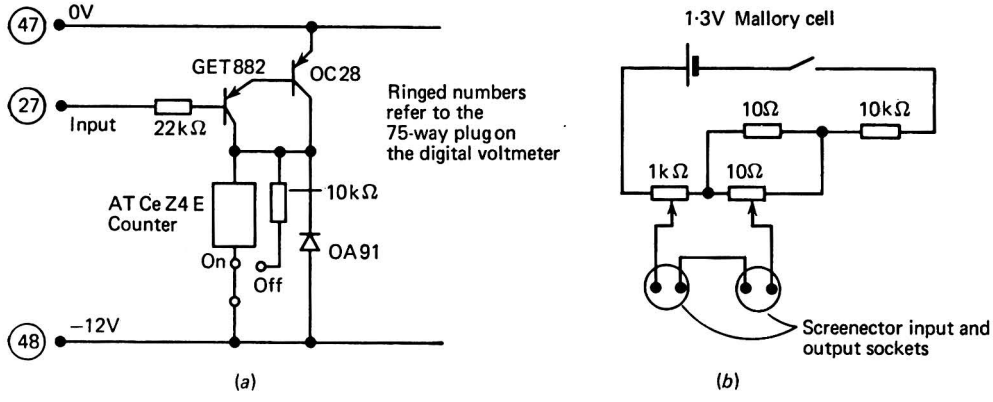

Fig. 4. Additions to Solartron digital voltmeter: (*a*), overload counter; and (*b*), backing-off voltage

METHOD OF OPERATION—

The digital voltmeter must first be set to operate as a voltmeter and the input voltage connected to give a positive polarity reading. This is because the voltmeter has its own polarity-sensing circuit and to function as an integrator it must be sensing positive. Thus to set up the voltmeter as an integrator the following procedure must be followed. Firstly, set the backing-off voltage to zero and switch it off, then set up the voltmeter to measure volts. Connect the input voltage via the backing-off voltage box to the input of the voltmeter. Adjust the polarity to be positive. At this stage, if used with the electrolytic hygrometer and set as described below, the voltmeter will read the actual p.p.m. of water to the nearest 0·01 p.p.m. Next, turn the Volts/Count switch to Count Manual, then set the Timer switch on the back of the voltmeter to Count, turn the Auto/Manual switch to Manual and switch on the backing-off voltage. If the voltmeter is not already counting, press the Manual Start push-button, following which it should start to count.

Slowly turn up the backing-off voltage. The counting rate should now begin to decrease. If it does not the polarity sensing circuit of the voltmeter has been reversed to negative; the voltmeter must therefore be set back to the Volts mode and the above procedure repeated. Adjust the backing-off voltage until the counter just ceases to operate at the input level corresponding to the base-line above which it is required to integrate, then switch on the electromagnetic counter and re-set it to zero.

Any increase in the input voltage will now cause the voltmeter to start counting, and as the hundreds numeral changes from 8 through 9 to 0 the electromagnetic counter will record 1 digit. When the input voltage has completed its cycle and returned to the base-line the counter will stop and the accumulated total will be proportional to the integral of the voltage *versus* time sequence. The counting can be stopped at any time and the voltmeter re-set to zero by operation of the Manual Start push-button.

The maximum frequency of the voltage-to-frequency converter is 2×10^5 pulses s^{-1}. As the electromagnetic counter can operate only up to less than 10 counts s^{-1}, corresponding to 10^4 pulses s^{-1}, it is the counter rather than the voltmeter that sets the maximum count-rate, and it is easy to hear when the limit is being approached.

When used with the electrolytic hygrometer the digital voltmeter can be connected (through the small box containing the counter and backing-off circuits) to the recorder socket of the hygrometer control box, and the recorder adjustment can be set so that full-scale deflection on the meter reads 10·00 mV on the voltmeter. As a better alternative, a special socket can be provided on the control box connected to a potential-dividing circuit, and this can be set so that a cell current of 132 μA (10 p.p.m. of water) on the 10-p.p.m. range reads 10 mV on the voltmeter. A recorder can then be used at the same time as the integrator if desired. (The same potential-dividing circuit should not be used for both the voltmeter and the recorder; if it is there will be some feedback from the recorder to the integrator which will affect the count-rate, especially at low levels.)

The 200-mV range is used for integrating, and it will be found that if the backing-off voltage is set to start counting at zero cell current the count-rate at full-scale deflection is 300 units min^{-1} on the electromagnetic counter. On the 10-p.p.m. range each of these units is theoretically equal to 0·002 45 μg of water, and the total capacity of the integrator (9999 units) is 24·5 μg. The last of the three digits on the voltmeter represents 2·5 pg of water; these digits are not, of course, normally recorded but they are very useful as they give an accurate indication of the exact moment when counting stops.

The electromagnetic counter continues to operate up to at least 1·6 times full scale; this is a useful feature when the peak that is being integrated happens to go a little off-scale on the meter, or the recorder, or both.

By the operation of four switches (the Volts/Count, Timer, Auto/Manual and backing-off voltage switches) the digital voltmeter is immediately converted back to the voltmeter mode so that it gives a digital reading with a precision of 0·01 p.p.m. (on the 10-p.p.m. range). This facility is very useful in checking the rate of change of a parts per million of water reading, or the level of an integrating base-line.

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Assay of Sodium Borohydride by Chloramine-T Oxidation

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An elegant and rapid method has been evolved for the assay of sodium borohydride by using chloramine-T as the oxidising agent.

A NUMBER of methods have been described in the literature for the assay of sodium borohydride. The method based on the decomposition of the hydride with an alcohol, water or dilute acid requires the use of a vacuum assembly.[1] In the direct titration of sodium borohydride solution with sodium hypochlorite, the pH of the solution during the titration is critical, and is maintained in the range 9·6 to 10·3 by making use of a carbonate buffer.[2] Titrimetric methods with iodine and potassium iodate as oxidants have also been described.[3,4] The present method involves the use of chloramine-T as the oxidising agent, which is more stable than sodium hypochlorite. The method is quite rapid, simple and reliable, and the results obtained agree with those obtained by the iodate method.

REAGENTS—

Analytical-grade reagents were used.

Standard chloramine-T solution,[5] 0·05 M—Dissolve 15 g of recrystallised chloramine-T in 500 ml of distilled water and filter the solution to remove any particulate matter. Dilute the filtrate to 1 litre and store it in an amber-coloured bottle. With a pipette, transfer 25 ml of chloramine-T solution into a 250-ml stoppered conical flask. Add 5 ml of 4 M hydrochloric acid, followed by 10 ml of 10 per cent. potassium iodide solution. Titrate the liberated iodine against a standard 0·1 M thiosulphate solution. Use starch solution as the indicator when near the end-point.

Standard thiosulphate solution, 0·1 M—Dissolve 25 g of sodium thiosulphate pentahydrate in 1 litre of carbon dioxide free distilled water containing 100 mg of sodium carbonate.

Standard potassium iodate solution, 0·033 M—Dissolve 7·134 g of dry potassium iodate in 1 litre of distilled water.

Potassium iodide solution, 10 *per cent.*—Dissolve 100 g of potassium iodide in 1 litre of distilled water.

Sodium borohydride solution—Dissolve between 200 and 500 mg of the sample in 250 ml of M sodium hydroxide solution. All transfer operations should be carried out in a dry-box in an atmosphere of nitrogen.

Dilute hydrochloric acid, 4 M.

Sodium hydroxide, 2 M *solution.*

Amylose starch indicator, 1 *per cent. solution.*

PROCEDURE—

Add an aliquot of the sodium borohydride solution (10 ml containing 8 to 20 mg of solid) to a known excess of chloramine-T solution (50 ml of solution *plus* 25 ml of 2 M sodium hydroxide solution) in a 250-ml stoppered conical flask. Shake the contents of the flask for 1 minute and then add 25 ml of potassium iodide solution. Acidify the contents by the addition of 25 ml of dilute hydrochloric acid. Titrate the liberated iodine against thiosulphate solution and then carry out a blank determination. The difference between the blank titration value and that of the sample under test will give the amount of the oxidant consumed by sodium borohydride.

RESULTS AND DISCUSSION

The analytical results are reproducible, as can be seen from the results presented in Table I. Two different samples, A and B, of sodium borohydride have been analysed by this method, and the results compare favourably with those obtained by the iodate method.

TABLE I

ASSAY OF SODIUM BOROHYDRIDE BY CHLORAMINE-T OXIDATION

Sodium borohydride sample*	Solvent	Chloramine-T method		Potassium iodate method	
		Mean, per cent.	Standard deviation, per cent.	Mean, per cent.	Standard deviation, per cent.
A	NaOH (M)	89·97	0·06	89·94	0·12
B	NaOH (M)	86·59	0·042	86·58	0·02
A	Dioxan	89·93	0·061	89·93	0·064
B	Dioxan	86·60	0·016	86·61	0·016

* A and B are two different samples of sodium borohydride (B.D.H.).

It can be seen that eight equivalents of chloramine-T are consumed by 1 mole of sodium borohydride according to the equation—

$$BH_4^- + 3H_2O \rightarrow H_2BO_3^- + 8H^+ + 8e$$

Thus, 1 ml of 0·05 M chloramine-T is equivalent to 0·4731 mg of sodium borohydride.

The present method can also be extended as follows to determine the amount of sodium borohydride dissolved in a non-aqueous solvent such as dioxan.

Shake 200 mg of sodium borohydride with 100 ml of dry dioxan in a nitrogen atmosphere for 2 hours in a dry-box. Filter the solution out of contact with air. Add a 10-ml aliquot of the resulting solution to an excess of chloramine-T solution (25 ml of solution *plus* 200 ml of M sodium hydroxide). Shake the contents for 1 to 2 minutes, dilute with 100 ml of water and determine the excess of chloramine-T after acidifying the contents as described earlier. Dioxan does not consume any chloramine-T, as indicated by a blank experiment. The analytical results compare favourably with those of the potassium iodate method. Such a procedure is thus suitable for the determination of the solubility of sodium borohydride in organic solvents. The amount of sodium borohydride in the dioxan solution is found to be 0·164 mg in 100 ml of the solvent at 25 °C.

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Determination of Microgram Amounts of Antimony, Bismuth, Lead and Tin in Aluminium, Iron and Nickel-base Alloys by Non-aqueous Atomic-absorption Spectroscopy*

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Microgram amounts of antimony, tin, lead and bismuth are extracted quantitatively from a 10 per cent. hydrochloric acid solution of the sample containing 2 per cent. of ascorbic acid and 6 per cent. of potassium iodide, in a single 30-s extraction, into a 5 per cent. solution of trioctylphosphine oxide in 4-methylpentan-2-one. The extract is then nebulised directly into the atomic-absorption burner flame.

Use of this technique permits the determination of as little as 0·1 p.p.m. of these metals. The general precision of the proposed method is 5 ± 0·3 p.p.m.

BECAUSE certain properties of metals and alloys may be critically dependent on the presence of trace amounts of minor constituents,[1–4] reliable analytical methods for determining these constituents at levels below 100 p.p.m. are important. The accurate determination of less than 50 p.p.m. of antimony, bismuth, lead and tin is time consuming by classical methods,[5] and difficult by direct instrumental techniques[6]; therefore, the use of concentration techniques is required.[7,8] Atomic-absorption spectroscopy is sometimes applicable to the direct determination of elements in the range of 5 to 100 p.p.m.; however, antimony, bismuth, tin and perhaps lead are among the metals the solutions of which must be concentrated to permit satisfactory determination by atomic absorption at these levels. The atomic-absorption response for lead is greater than that for the other three elements and direct determinations have been reported with practical limits of detection of 20 p.p.m.[9] and even 2·5 p.p.m.[10]

A satisfactory co-precipitation procedure has been developed for the concentration of these elements that is applicable to nickel and copper-base systems[11]; however, its application to iron-base alloys is limited. Another system for this concentration could be based on the solvent extraction of the metals with an oxonium-type solvent. The formation of an extracted oxonium species depends on the combined action of the associated anion and the oxygen-containing organic compound to displace the co-ordinated water from the metal.[12] Examples of oxonium-type solvents are alcohols, ethers,[13] ketones[14,15] and phosphine oxides.[16] Generally, ketones are more efficient metal extractants than ethers, and phosphine oxides are even more efficient.

Kitahara[17] found that antimony and tin, together with cadmium, gold, mercury and thallium, were completely extracted with diethyl ether from a 6·9 M hydriodic acid solution. He reported that lead, iron(II), nickel, cobalt, chromium, manganese, titanium, zirconium and aluminium were not extracted, and found a 34 per cent. extraction for bismuth. Irving and Rossotti[18] also studied the extraction of metal iodides with diethyl ether from a 1·5 M solution of potassium iodide in 1·5 N sulphuric acid. They found that tin was completely extracted and antimony partly extracted, but that bismuth and lead were not extracted. West and Carlton[19] used 4-methylpentan-2-one (methyl isobutyl ketone; MIBK) and a 5 per cent. hydrochloric acid solution containing an excess of potassium iodide and found that lead was completely extracted and that antimony and tin were only partly extracted. Kakita and Gotô[20] found that with the appropriate concentrations of potassium iodide with either sulphuric or hydrochloric acid the following percentage extractions were obtained: antimony 99·4, bismuth 99·9 and lead 95. No quantitative results were given for tin. Luke[21] reported that lead, bismuth and antimony can be almost quantitatively extracted from a 5 per cent. hydrochloric acid solution containing iodide, providing a double extraction with MIBK is performed.

* Presented at the Pittsburgh Conference, Cleveland, Ohio, March 1, 1971.

The organic solvents discussed above were used without an inert diluent; however, for trioctylphosphine oxide (TOPO), which is a solid, a diluent is required. Ishimori, Kimura, Fujino and Murakami[22] used a 5 per cent. solution of TOPO in toluene and studied the extraction of most elements as a function of the hydrochloric acid concentration. With M hydrochloric acid they reported that iron(II), nickel, cobalt, manganese, chromium(III), antimony and lead were not extracted. Under the same conditions they reported complete extraction of bismuth and tin as well as of uranium, gold, zinc and mercury. No results are available for the extraction of metal iodides by TOPO.

In two other methods non-aqueous atomic-absorption spectroscopy was used for the determination of lead[23] and bismuth[24] in ferrous alloys. The development of a rapid and accurate atomic-absorption method is described here for the determination of microgram amounts of antimony, bismuth, lead and tin. A 5 per cent. solution of TOPO dissolved in MIBK is used to concentrate the elements prior to their determination by non-aqueous atomic-absorption spectroscopy.

Experimental

Apparatus—

A Perkin-Elmer, Model 303, atomic-absorption spectrophotometer, equipped with a premix chamber and triple-slot Boling and nitrous oxide heads, was used. Perkin-Elmer hollow cathodes were used as source lamps and a Sargent, Model SRG, recorder was used as a read-out device. The instrument settings are summarised in Table I, the instrumental response being optimised according to the manufacturer's instructions.

Table I

Operating conditions for Perkin-Elmer 303 atomic-absorption spectrophotometer when aspirating MIBK solutions

Element	Wave-length/nm	Slit width/nm	Lamp current/mA	Working range/μg ml^{-1}	Gas flow-rates/l min^{-1}		
					C_2H_2 at 8 p.s.i.g.	Air at 30 p.s.i.g.	N_2O at 30 p.s.i.g.
Antimony	217·6	0·2	35	1 to 20	2	24	—
Bismuth	223·1	0·2	30	1 to 10	2	24	—
Lead	217·0	0·7	30	1 to 7	2	24	—
Tin	286·3	0·7	30	1 to 50	2	—	12

Reagents—

Non-aqueous standards—A stock solution containing 1000 μg ml^{-1} of antimony, bismuth, lead and tin is prepared as follows (see Table II). Dissolve 0·4367 g of dibutyltin bis-(2-ethylhexanoate), 0·2632 g of lead cyclohexanebutyrate, 0·2585 g of triphenylbismuth and 0·2900 g of triphenylstibine in 10 ml of 2-ethylhexanoic acid *plus* 20 ml of MIBK. Dilute to 100 ml with MIBK. A dilute solution is prepared from the stock solutions by dilution with MIBK to contain 50 μg ml^{-1} of the test elements. A precipitate appeared 2 weeks after preparation of the stock and dilute solutions if 2-ethylhexanoic acid was not present.

Standard stock solution, 1000 μg ml^{-1}—Prepare a stock solution from high purity metals containing all the elements of interest. It should be 6 M in hydrochloric acid to prevent hydrolysis.

Table II

Compounds used to prepare a non-aqueous standard stock solution

Organometallic compound	Molecular weight	Metal, per cent. (certified)	Source
Dibutyltin bis(2-ethylhexanoate)	519·3	Sn 22·9	Eastman* 10427
Lead cyclohexanebutyrate	545·7	Pb 38·0	Eastman 10395
Triphenylbismuth	440·3	Bi 38·7†	Eastman 2442
Triphenylstibine	353·1	Sb 34·8†	Eastman 1553

* Eastman Organic Chemicals, Rochester, New York 14650, U.S.A.
† Metal content calculated for pure compound.

TOPO, 5 per cent. solution in MIBK—Dissolve 12·5 g of TOPO (Eastman 7440) in 250 ml of MIBK.

Iodide reagent—Prepare daily a solution containing 30 per cent. w/v of potassium iodide and 10 per cent. w/v of ascorbic acid in 10 per cent. v/v hydrochloric acid.

All chemicals used were of analytical-reagent grade. Grade A calibrated glassware was used.

PROPOSED PROCEDURE—

Weigh accurately into beakers samples that contain a sufficient amount of antimony, bismuth, lead and tin to give a satisfactory signal (see Table I). Instrumental response can be varied by adjusting the sample weight and volume of extractant as shown by the following example for the 10-p.p.m. level:

Sample weight/g	1	1	5	5
Final volume/ml	10	5	5	2
Element/μg ml^{-1}	1	5	10	25

Prepare a reagent blank. Dissolve the sample and remove any oxidant used in the sample preparation (see Table III). Rinse the sides of the beaker with about 5 ml of water and add 4 g of ascorbic acid to those samples that contain iron(III). The disappearance of the dark yellow colour caused by iron(III) chloride is used to judge the completeness of the reduction to iron(II). Add 15 ml of the iodide reagent and transfer the sample to a 150-ml separating funnel, rinsing the beaker with water, and adjust the final volume to about 50 ml. With a pipette, introduce 10 ml of the 5 per cent. TOPO - MIBK reagent into the separating funnel, equilibrate the solutions for 30 s, and allow the phases to separate. Drain off the lower aqueous layer and discard it. Transfer the organic phase into a 15-ml stoppered vial. Occasionally an emulsion forms, which can be broken by briefly centrifuging the organic phase. Do not use phase-separation paper to break the emulsion unless it has been found to be free from a tin compound that is soluble in MIBK.

TABLE III

SAMPLE PREPARATION SCHEME FOR SOLVENT EXTRACTION

Matrix	Solvent (ml of acid) 1 g	5 g	10 g	Final preparation for 1-g sample (graphite and silica removed by filtration)
Aluminium	HCl (15) + 30% H_2O_2*	HCl (30) + 30% H_2O_2	HCl (60) + 30% H_2O_2	Evaporate to 5 ml of HCl
Iron	HCl (15) + HNO_3 (5)	HCl (30) + HNO_3 (10)	HCl (60) + HNO_3 (20)	Evaporate to 5 ml of HCl 10 ml of HCl + heat + HCOOH*; evaporate nearly to dryness and add 5 ml of HCl
Nickel	HNO_3 (10) + 10 ml of H_2O	HNO_3 (30) + 30 ml of H_2O	HNO_3 (60) + 60 ml of H_2O	10 ml of HCl + heat + HCOOH; evaporate nearly to dryness and add 5 ml of HCl
Nickel oxide	HCl (15)	HCl (30)	HCl (60)	Reduce volume to 5 ml
Fe - Ni - Cr alloys	HCl (15) + HNO_3 (5)	HCl (30) + HNO_3 (10)	HCl (60) + HNO_3 (20)	10 ml of HCl + heat + HCOOH; evaporate nearly to dryness and add 5 ml of HCl

* H_2O_2 and HCOOH are added dropwise, the latter until brown fumes due to the oxides of nitrogen disappear.

Optimise the burner height, aspiration rate and gas flow-rates; the conditions given in Table I can be used as guide-lines. Prepare calibration solutions by diluting the standard stock solution with MIBK. Beginning with the solution that has the lowest metal content aspirate each solution and record its absorbance. Aspirate the sample solutions and blank and record their absorbances. Correct the absorbance readings of the samples for any blank. Convert the absorbance of the test solution into micrograms per millilitre by using the appropriate calibration graph and calculate the levels of antimony, bismuth, lead and tin.

Discussion and results

Substantiation of the proposed method—

The findings given in the literature previously discussed suggest that extraction from a hydrochloric acid medium with TOPO[22] followed by extraction of the iodides with MIBK[21,25] should permit the quantitative separation of these four elements. The initial attempts in this laboratory to concentrate the solutions of these elements gave results that were essentially in agreement with those previously reported. With MIBK less than 10 per cent. of these four elements are extracted from a hydrochloric acid medium, while with a 5 per cent. solution of TOPO in cyclohexane, bismuth and tin are completely extracted. More than 90 per cent. of the antimony, bismuth and lead is extracted, by a single equilibration with 10 ml of MIBK, from 10 per cent. hydrochloric acid in the presence of an excess of potassium iodide. In the proposed procedure a 5 per cent. solution of TOPO in MIBK is used to rapidly concentrate antimony, bismuth, lead and tin into a small volume. The separation can be performed in a single equilibration, and decomposition of the organic phase is avoided by direct aspiration of the extract into the flame. Previously, a convenient and direct separation of these four elements has not been possible. A reliable spectrophotometric procedure that enables an iron or copper matrix to be separated before the extraction of dihydrogentetraiodolead(II) with MIBK from a 5 per cent. solution of hydrochloric acid containing 7 per cent. of potassium iodide[26,27] has been applied to the determination of trace amounts of lead by non-aqueous atomic absorption.[28]

Table IV

Verification with atomic absorption of the extraction of antimony, bismuth, lead and tin

Experimental conditions—organic phase: 10 ml of 5 per cent. TOPO in MIBK; aqueous phase: 50 ml of 10 per cent. HCl, 6·5 g of KI and 1·5 g of ascorbic acid

A. *Recovery of the proposed extraction as compared with "standard" organometallic compounds dissolved in MIBK—*

Method	Absorbance for 10 μg ml^{-1} in MIBK			
	Antimony	Bismuth	Lead	Tin
Extraction	0·208	0·398	0·602	0·056
Organometallic standard	0·208	0·409	0·585	0·051

B. *Recovery of the extracted elements after acid decomposition of the organic material—*

	Antimony	Bismuth	Lead	Tin
Added/μg	200	200	200	200
Found/μg	210	193	200	200

The proposed procedure is not an empirical technique. The validity of the TOPO - MIBK separation has been verified by two methods, as shown in Table IV. The test elements were added at the 100 and 200-μg levels for convenience of measurement; however, the conclusion is equally valid at lower levels. The recovery should be verified before extrapolating this technique to levels above 500 μg because initial tests showed 75 per cent. recovery for tin when a 0·1 per cent. solution of TOPO in MIBK was used instead of a 5 per cent. soluti n *i.e.*, higher levels could almost certainly be determined if the concentration of TOPO is increased. The solutions of organometallic compounds that were used as "standards" in Table IV are described in Table II (also see Reagents); they were diluted with MIBK to bring the metal content to 10 μg ml^{-1}. The antimony and bismuth organometallic compounds are not certified standard materials; however, even a 1 per cent. error in the theoretical metal content would alter the final results for concentration by only about 0·3 μg ml^{-1}. Comparison of the absorbance values for the extraction procedure with those obtained by dissolving the organometallic compounds shows a slight difference. TOPO is not present in the organometallic standards but the results obtained show no appreciable change in the response as the TOPO concentration in MIBK increases from 0 to 5 per cent. The results given in Table IV A also serve to "certify" the metal content of the organometallic compounds, that is, these compounds are now useful as "secondary standards" that can be used to prepare dilute solutions for non-aqueous atomic-absorption spectroscopy. The quantitative nature of the separation was also verified by destroying the organic phase and taking up the extract in aqueous media for analysis by atomic absorption (Table IV B).

SENSITIVITY—

The use of organic solvents in the determination of trace levels of metals by atomic-absorption spectroscopy increases the instrumental response as a result of the improved efficiency in the process of introducing the metals into the flame. Different organic solvents have been studied for the determination of lead in petrol[29] and they show improved response compared with the use of aqueous media. For the proposed extraction procedure the increases in response are as follows: antimony 4, bismuth 12, lead 8 and tin 2-fold, compared with aqueous media. The increase in sensitivity for lead extracted into MIBK has also been reported to be 5 to 6-fold.[28]

INTERFERENCES—

The proposed 5 per cent. TOPO - MIBK extractant is a useful mixed solvent for several reasons. First, the extraction of antimony, bismuth, lead and tin is essentially complete while less than 1 per cent. of aluminium, calcium, chromium, cobalt, iron(II), magnesium, manganese, molybdenum, nickel, titanium and vanadium is extracted. Cadmium, copper, gold, indium, mercury, thallium and zinc are at least partly extracted; however, no interference should be expected from these elements because, with the exception of copper and zinc, they will not generally be present in aluminium, iron or nickel-base alloys. In addition to separating the required elements from a variety of matrices the extraction is nearly an ideal pre-concentration system.[30] Secondly, precise control of the extraction variables is not required as it is when MIBK alone is used to extract a metal iodide. The concentration of hydrochloric acid can vary from 4 to 20 per cent. v/v and the level of potassium iodide from 0·6 to 7·5 g per 50 ml. Even the total volume of aqueous phase can vary from 25 to 200 ml, provided that a calibration curve is prepared under the same conditions. Small variations in the volume of the aqueous phase are not important but large variations affect the final volume of the organic phase because of the solubility of the MIBK in dilute hydrochloric acid. Precise control of the equilibration time is not required because the extraction can be completed in 5 s, even when the volume of the extractant is reduced to 3 ml. This concentration is useful because it permits the analysis of a sample at the 1-p.p.m. level, by taking a 10-g sample and concentrating the solution of the elements to be determined to 3 ml, thus giving a final concentration of 3·3 μg ml^{-1}. Once the extraction has been performed, the phases have been separated and the organic phase protected from evaporation, the extract is stable for at least several days and need not be aspirated into the flame immediately after extraction.

The third advantage of the proposed extractant is its relative freedom from interference. Copper could be expected to interfere. The results obtained show that 100 μg of antimony, bismuth, lead and tin can be determined in the presence of as much as 50 mg of copper without interference. Under the experimental conditions used any level of copper greater than 0·1 g gives a precipitate of copper(I) iodide and low results are obtained for all elements. Other procedures for the analysis of copper-base alloys are available.[11,28] Nitric acid remaining after the dissolution causes the organic phase to become dark and viscous and to give low results. Several approaches were used to remove nitric acid but the best technique is that in which formic acid is used to decompose the nitrate and then the excess of formic acid is removed by evaporation with hydrochloric acid. Small amounts of formic or nitric acid were found not to interfere. Iron(III) must not be present; however, no interference is encountered from iron(II) or the large amounts of ascorbic acid used to reduce iron(III). Even 10 g of iron(II) does not cause interference. Occasionally an emulsion is formed with some samples, which can be broken either by filtration or centrifugation.

The presence of other acids, in addition to hydrochloric acid, might be useful if they do not hinder the extraction. For instance, hydrofluoric acid could be added before the extraction to volatilise fluorosilicic acid, while sulphuric and phosphoric acids could be used to keep elements such as molybdenum, niobium and tungsten in solution. Complete recovery of all four elements was obtained when the extraction medium was made 2 per cent. in either sulphuric or phosphoric acid. The presence of perchloric acid gave results that were 34 per cent. low for lead and about 5 per cent. low for the other elements. A solution containing hydrofluoric and boric acids gave low results for antimony and tin while the recovery of bismuth and lead was quantitative.

TABLE V

NON-AQUEOUS ATOMIC-ABSORPTION RESULTS ON CERTIFIED STANDARDS OBTAINED AFTER THE TOPO - MIBK EXTRACTION OF ANTIMONY, BISMUTH, LEAD AND TIN

Designation	Matrix	Antimony, p.p.m.		Bismuth, p.p.m.		Lead, p.p.m.		Tin, p.p.m.	
		Certified	Found	Certified	Found	Certified	Found	Certified	Found
N.B.S. 85b	Aluminium alloy	—	31	—	22	210	202	—	<35
N.B.S. 87a	Aluminium alloy	—	42	—	28	1000	960	500	504
B.C.S. 320	Mild steel	(30)	31	—	9	—	10	850	852
B.C.S. 321	Mild steel	(40)	25	—	9	—	8	140	140
B.C.S. 322	Mild steel	(40)	28	—	7	—	8	2400	2372
B.C.S. 323	Mild steel	(40)	30	—	8	—	7	240	226
B.C.S. 324	Mild steel	(40)	32	—	18	—	19	1300	1328
B.C.S. 325	Mild steel	20	23	—	7	—	9	460	443
B.C.S. 326	Mild steel	50	53	—	10	140	145	—	33
B.C.S. 327	Mild steel	330	313	—	12	100	108	—	44
B.C.S. 328	Mild steel	260	268	—	16	150	162	—	46
B.C.S. 329	Mild steel	180	183	—	40	500	526	—	57
B.C.S. 330	Mild steel	180	169	—	10	30	36	—	46
B.C.S. 337	Austenitic stainless steel	—	22	—	4	12	14	—	153
N.B.S. 1161	Low-alloy steel A	—	21	—	8	(30)	36	220	210
N.B.S. 1162	Low-alloy steel B	—	22	—	5	60	62	660	620
N.B.S. 1163	Low-alloy steel C	—	46	—	14	120	123	130	129
N.B.S. 1164	Low-alloy steel D	—	44	—	15	200	204	430	418
N.B.S. 1166	Low-alloy steel F	—	12	—	3	(13)	19	50	48
N.B.S. 1167	Low-alloy steel G	—	13	—	3	6	6	1000	1019
N.B.S. 1174	White cast iron—1	1900	1852	(80)	87	(100)	102	2300	2381
N.B.S. 1175	White cast iron—2	200	135	(170)	162	30	30	250	213
N.B.S. 19g	Acid open-hearth steel	—	11	—	6	—	9	80	83
N.B.S. 65d	Basic electric steel	—	8	—	8	—	12	40	36
B.C.S. 239/3	Carbon steel	—	59	—	20	—	24	300	305
No. 41	"B-1900" (see ref. 8)	—	10	(<0·5)	2	(6·2 ± 2)	6	(10)	10
No. 42	"B-1900"	—	10	(<0·5)	6	(6·0 ± 1)	6	(15)	33
N.B.S. 361	AISI 4340 steel	42	42	(5)	8	(<1)	1	110	102
N.B.S. 362	AISI 94B17 steel (modified)	130	100	(60)	27	(6)	6	(160)	180
N.B.S. 365	Electrolytic iron	(<0·5)	<1	(<0·1)	2	(<0·5)	<1	(<5)	3
B.C.S. 242/1	Ferro-tungsten	—	<1	—	6	—	6	340	329

Values in parentheses not certified.

TABLE VI

COMPARISON OF SEPARATION METHOD FOR THE DETERMINATION OF ANTIMONY, BISMUTH, LEAD AND TIN BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

Designation	Matrix (element, p.p.m., provisional value)	Found, p.p.m.									
		Antimony		Bismuth			Lead			Tin	
		MnO_2	TOPO	MnO_2	MIBK	TOPO	MnO_2	MIBK	TOPO	MnO_2	TOPO
N.B.S. 1159	Electronic alloy; Ni 48, Fe 51	6	5	10	8	5	9	8	10	31	25
N.B.S. 1160	Magnetic alloy; Ni 80, Fe 19	9	8	7	7	8	18	19	19	10	20
PDMRL RL 17699	Ferro-nickel	62	69	2	–	4	4	–	6	4	10
PDMRL RL 15710	Pig nickel	8	6	3	–	10	10	–	13	13	13
HAPD E 3923	Incoloy* alloy 800	14	10	9	6	5	4	6	6	13	18
HAPD E 3924	Incoloy alloy 800	10	14	8	5	4	6	6	7	17	23
HAPD E 3925	Incoloy alloy 800	15	14	2	7	4	6	4	7	22	25
HAPD E 3926	Incoloy alloy 800	11	14	2	6	4	7	–	7	21	25
HAPD E 3927	Incoloy alloy 800	11	18	2	6	6	4	4	6	11	15
HAPD E 3928	Incoloy alloy DS	<1	6	1	–	4	3	–	6	4	10
HAPD E 3929	Incoloy alloy DS	<1	10	1	–	5	6	–	7	7	20
HAPD E 3930	Incoloy alloy DS	12	10	1	–	7	5	4	8	12	20
HAPD E 3931	Incoloy alloy DS	<1	12	2	–	–	4	–	7	2	25
HAPD E 3932	Incoloy alloy DS	2	10	<1	–	5	4	–	7	9	25
HAPD B 7047	Inconel* alloy X750	4	6	1	3	6	4	6	8	4	10
HAPD B 7048	Inconel alloy X750	14	15	1	5	4	6	–	6	<1	10
HAPD B 7049	Inconel alloy X750	14	15	<1	3	5	2	11	6	7	5
HAPD B 7050	Inconel alloy X750	4	8	5	–	5	12	–	6	5	5
HAPD B 7051	Inconel alloy X750	6	6	6	2	8	4	9	8	<1	5
PDMRL RL 428	Maraging steel	16	19	1	3	4	7	4	7	42	65
PDMRL RL 429	Maraging steel	12	15	4	5	4	6	5	4	37	60
B.C.S. 310	Nimonic* 90	11	6	4	3	2	12	13	8	30	28
PDMRL RL 22830	Cast stainless steel	–	16	–	–	5	26	–	27	–	35
PDMRL SR 18363	Nickel	47	70	4	2	4	5	2	7	19	19
B.C.S. 371	Commerical nickel	5	6	2	–	6	28	–	25	10	<1
N.B.S. 671	Nickel oxide (Pb 16) (see ref. 11)	3	<1	3	<1	<1	16	20	16	8	2
N.B.S. 672	Nickel oxide (Pb 39)	1	<1	2	3	<1	39	41	38	5	2
N.B.S. 673	Nickel oxide (Pb 3)	3	<1	<1	3	<1	7	4	4	<3	2
PDMRL C 59981	Ni electrode (Pb 1 to 10, Sn 1 to 10)	2	2	1	–	7	2	–	2	3	1
HAPD N 4379a	Nickel 200	<0·5	<0·5	0·5	–	0·5	6	–	9	0·2	2
HAPD N 4361a	Nickel 200	2	<0·5	1	–	<0·5	6	–	7	0·2	<1
HAPD N 2930a	Nickel 200	3	<0·5	1	–	<0·5	8	–	10	0·2	5
HW F 292	Nickel 200	1	<0·5	1	–	0·5	0·8	–	2	<0·1	<1
HW F 293	Nickel 200	<0·2	<0·5	0·3	–	0·5	0·8	–	2	0·1	<1
HW F 294	Nickel 200	<0·2	<0·5	1	–	0·5	0·8	–	2	<0·1	<1
HW F 295	Nickel 200	0·8	<0·5	0·7	–	0·5	1	–	2	<0·1	<1
HW F 296	Nickel 200	<0·2	<0·5	0·7	–	<0·5	1	–	2	<0·1	<1
HW F 297	Nickel 200	1	<0·5	1·5	–	<0·5	3	–	2	<0·1	<1

* Incoloy, Inconel and Nimonic are registered trademarks of the International Nickel Company, Inc.

ACCURACY AND PRECISION—

All the results indicate that antimony, bismuth, lead and tin can be determined by the proposed method without interference, except from large amounts of copper and zinc. It was not possible to use certified standard reference materials to verify the method for all elements at levels below 100 p.p.m., as such materials do not exist. The results obtained by the proposed method on the few standards that are available are given in Table V. Several of the B.C.S. mild steels have previously been analysed for lead by atomic absorption after extraction.[27] The average of the results obtained by Dagnall *et al.*[27] for lead compares more favourably with the results of the proposed method given in Table V, *i.e.*, relative to the certified values: B.C.S. 326, 143 p.p.m.; B.C.S. 327, 118 p.p.m.; B.C.S. 328, 160 p.p.m.; B.C.S. 329, 513 p.p.m.; and B.C.S. 330, 40 p.p.m.[27]

The alloys designated Nos. 41 and 42 are nickel-base superalloys that contain as much as 4 per cent. of tantalum, 1 per cent. of titanium and 6 per cent. of molybdenum, constituting fairly high levels of hydrolysable elements. The results are not low compared with the results given in parentheses, which are an average obtained as a result of an inter-laboratory study[8]; therefore, the likelihood of some co-precipitation of metals such as lead on the acid-insoluble elements is small. Similarly, the result for B.C.S. 242/1, which contains 82 per cent. of tungsten, shows good agreement with the certified value for tin, especially when the range of values used for certification is considered (0·027 to 0·039 per cent. of tin). The

TABLE VII

DETERMINATION OF ANTIMONY, BISMUTH, LEAD AND TIN BY NON-AQUEOUS ATOMIC ABSORPTION AFTER SEPARATION FROM VARIOUS REFERENCE MATERIALS WITH TOPO - MIBK

Designation	Matrix	Found, p.p.m. Antimony	Bismuth	Lead	Tin
N.B.S. 1185	High temperature alloy (AMS 5360A)	16	4	9	96
N.B.S. 1190	Udimet* 500	8	6	6	16
N.B.S. 1193	High temperature alloy (W 595)	71	6	6	14
N.B.S. 1194	High temperature alloy (A 286)	8	5	8	97
N.B.S. 1195	Discaloy† 24	35	8	12	52
N.B.S. 1204	Alloy 731 B	12	6	7	39
N.B.S. 1205	Alloy 731 C	12	7	6	50
N.B.S. 1156	Maraging steel	5	3	4	<1
PDMRL T 37559	Maraging steel	5	3	8	5
PDMRL T 37560	Maraging steel	112	114	50	111
PDMRL T 37561	Maraging steel	194	211	91	208
PDMRL T 37562	Maraging steel	468	322	123	529
PDMRL T 37563	Maraging steel	1050	1012	244	1165
PDMRL 73	Maraging steel	11	7	14	5
PDMRL 74	Maraging steel	13	7	8	4
PDMRL 75	Maraging steel	13	7	12	<1
N.B.S. 168	Co 41, Mo 4, Nb 3, Ta 1, W 4 alloy	14	8	16	111
N.B.S. 169	Ni 77, Cr 20 alloy	14	9	16	8
N.B.S. 349	Ni 57, Co 14, Cr 20 alloy	18	9	10	59
N.B.S. 160b	Cr 18, Ni 14, Mo 3 steel	28	5	18	90
N.B.S. 348	Ni 26, Cr 15 steel	20	6	10	76
N.B.S. 339	Cr 17, Ni 9, Se steel	28	8	14	134
N.B.S. 346	Cr 22, Ni 4, Mn 9 steel	23	6	15	89
PDMRL V 91109	IN 102	15	6	13	34
PDMRL T 44865	Ni - Cu - Nb steel	20	5	25	55
PDMRL T 42144	Stainless steel	20	6	8	<1
B.C.S. 218/3	Carbon steel	86	24	24	420
N.B.S. 65d	Basic electric steel	8	8	12	36
N.B.S. 32e	Ni - Cr steel	16	<1	112	122
N.B.S. 101e	Cr 18, Ni 9 steel	32	2	22	223
N.B.S. 55e	Ingot iron	14	2	3	44
N.B.S. 838	Mo high-speed tool steel	24	6	8	75
N.B.S. 840	Special W high-speed tool steel	14	2	6	160

* Udimet is a registered trademark of Special Metals Inc.
† Discaloy is a registered trademark of Westinghouse Electric Corporation.

validity of this assumption was checked in the presence of a series of synthetic alloys containing 70 per cent. of iron and 30 per cent. of one of the following elements: niobium, tantalum, molybdenum, titanium, zirconium and vanadium. Results were high for bismuth in the presence of molybdenum, for lead in the presence of titanium and niobium, and for tin in the presence of titanium. The high results are doubtless caused by impurities resulting from the matrix element being studied. Low results were obtained only for antimony in the presence of titanium.

The values in Table VI give a comparison of atomic-absorption results obtained after separation by the manganese(IV) oxide method,[11] the proposed TOPO - MIBK non-aqueous method and another MIBK extraction method.[31] In the last method the iodides are extracted, the organic matter is destroyed and the residue taken up in hydrochloric acid before aspirating the sample into the flame.

Results are presented in Table VII for the proposed method when applied to several types of alloys. The N.B.S. standard 55e has not been certified for its antimony, bismuth or lead content. The tin level is certified at 70 p.p.m. with a range of ± 100 p.p.m. reported for the three certification values. This ingot iron has been used for a precision study of the proposed method and additional information on its accuracy is of interest. Antimony was determined by atomic absorption after concentration with manganese(IV) oxide,[11] and a value of 17 p.p.m. was found; it was also determined by an extraction - spectrophotometric procedure involving the use of Brilliant green,[32] which gave a value of 15 p.p.m. None of the materials listed in Tables V, VI or VII has been completely certificated for all four elements; therefore, all the data given will be useful in establishing secondary instrumental standards.

Most of these materials are commercially available. N.B.S. materials are available from the U.S. Department of Commerce, National Bureau of Standards, Washington, D.C. 20234, U.S.A., and B.C.S. materials from the Bureau of Analysed Samples Ltd., Newham Hall, Middlesbrough, Teesside; those designated HAPD from Huntington Alloy Products Division, The International Nickel Company, Inc., Huntington, West Virginia 25720, U.S.A., and those HW from Henry Wiggin and Company Limited, Hereford. Materials designated PDMRL are internal secondary standards and are not commercially available.

Table VIII

Precision of the proposed method

	Found, p.p.m. $\pm \sigma$						
	Complete procedure				Calibration graph points (n = 50)		
Element	B.C.S. 337 (n = 15)	N.B.S. 55e (n = 20)	Ni 200 PDMRL T 53155 (n = 10)	For 10 μg ml^{-1} No matrix (n = 20)	1 μg ml^{-1}	5 μg ml^{-1}	10 μg ml^{-1}
Antimony	$22{\cdot}3 \pm 2{\cdot}6$	$13{\cdot}8 \pm 2{\cdot}7$	$11{\cdot}9 \pm 1{\cdot}2$	$9{\cdot}9 \pm 0{\cdot}5$	$1{\cdot}3 \pm 0{\cdot}3$	$5{\cdot}1 \pm 0{\cdot}2$	$10{\cdot}3 \pm 0{\cdot}2$
Bismuth	$1{\cdot}8 \pm 1{\cdot}2$	$1{\cdot}8 \pm 0{\cdot}6$	$9{\cdot}9 \pm 0{\cdot}6$	$10{\cdot}1 \pm 0{\cdot}4$	$1{\cdot}0 \pm 0{\cdot}1$	$5{\cdot}1 \pm 0{\cdot}1$	$10{\cdot}2 \pm 0{\cdot}2$
Lead	$13{\cdot}5 \pm 0{\cdot}8$	$3{\cdot}2 \pm 0{\cdot}5$	$11{\cdot}5 \pm 0{\cdot}3$	$10{\cdot}0 \pm 0{\cdot}2$	$1{\cdot}0 \pm 0{\cdot}05$	$5{\cdot}2 \pm 0{\cdot}07$	$10{\cdot}2 \pm 0{\cdot}1$
Tin	$51{\cdot}6 \pm 1{\cdot}8$	$43{\cdot}5 \pm 5{\cdot}3$	$8{\cdot}5 \pm 2{\cdot}2$	$9{\cdot}9 \pm 0{\cdot}7$	$1{\cdot}0 \pm 0{\cdot}4$	$5{\cdot}4 \pm 0{\cdot}4$	$10{\cdot}3 \pm 0{\cdot}5$

n = Number of determinations.

The results given in Table VIII show the precision of the proposed method for iron and nickel matrices in contrast with the precision of the instrumental measurement at 1, 5 and 10 μg ml^{-1}. The precision with which antimony, bismuth, lead and tin can be determined in this particular nickel 200 (99 per cent. of nickel) standard has already been demonstrated for atomic absorption in an aqueous medium, after concentration with manganese(IV) oxide.[11] The difference in the precision can be attributed mainly to improved sensitivity in non-aqueous media relative to aqueous media. The sample weights (1 g) and final dilution volumes (10 ml) used were the same for both sets of results; however, the average precision for antimony, bismuth and lead is eight times better for the proposed extraction procedure compared with the co-precipitation procedure. The proposed procedure is capable of precise analysis at the 1 p.p.m. level by taking a 10-g sample and concentrating the solution of the trace elements to give a final volume of 5 ml.

Lead has been determined spectrophotometrically in stainless steel B.C.S. 337 after extraction of the lead - dithizone complex from an ammoniacal citrate - cyanide solution.[33] The precision with this method is essentially the same as that given in Table VIII for the proposed method.

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The Effect of Various Acids on the Atomic Absorption of Rare Earths

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The effects of hydrochloric, sulphuric, nitric and perchloric acids on the atomic absorption of the rare earth elements yttrium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium have been determined. The rare earths can be categorised into two groups according to their behaviour in the four acids. Elements in group I (samarium, europium, dysprosium, holmium, erbium, thulium and ytterbium) showed little change in absorption behaviour in these acids, and no change when the acid concentration was varied from 0·1 to 0·5 M. Yttrium, gadolinium and terbium of group II are sensitive to the type of acid used. Considerable suppression of absorption was caused by sulphuric acid and less severe suppression by nitric acid. The suppression caused by sulphate and nitrate cannot be eliminated with enhancing agents, and these anions should be removed when the above elements are determined. The elements in group II can be determined in 0·1 to 0·5 M hydrochloric or perchloric acid.

IN recent years rare earths have become increasingly important in the development of electronics materials. Some of these materials are phosphors ($Y_{0·80}Yb_{0·19}Er_{0·01}F_3$, $Gd_{0·65}Yb_{0·35}Tm_{0·001}F_3$, etc.) that are used to convert infrared into visible radiation, which have application as solid-state lamps in numerical display indicators, and rare earth orthoferrites ($YFeO_3$, $Sm_{0·55}Tb_{0·45}FeO_3$, etc.) and "super garnets" ($Gd_{2·31}Tb_{0·60}Eu_{0·09}Fe_5O_{12}$, $Gd_{0·94}Tb_{0·75}Er_{1·31}Al_{0·5}Fe_{4·5}O_{12}$, etc.), which play an important rôle in the cylindrical magnetic domain devices. The quantitative analysis of these materials involves the determination of several rare earths in the same solution. As the chemical properties of rare earths are similar, classical wet-chemical techniques cannot be used; on the other hand, atomic-absorption spectroscopy is well suited to this purpose. Although the determination of europium in europium-activated orthovanadate phosphors has been reported by Manning[1] and Scott,[2] the papers occurring in the literature on the determination of rare earths by atomic-absorption spectroscopy emphasise primarily the detection limits[3] and the extension of these limits.[4] Because the amounts of individual rare earths in the materials indicated above can vary from less than 1 per cent. to more than 50 per cent., precision and accuracy rather than limits of determination are the most important factors. The precision of the determination is dependent largely on instrumental factors and on the accuracy achieved in the matching of the matrix of the standard solutions to the matrix of the sample solutions. To optimise analytical conditions cations were added to the standards in the same concentrations as those found in the sample solutions. The type of anion and its concentration in the sample solution are dependent on the type of acid used to dissolve the material. While most complex rare earth oxides are soluble in 6 M hydrochloric acid, the recrystallised fluorides can be dissolved only in concentrated sulphuric or perchloric acid. Because of the similarity of the chemical properties of rare earths one would expect that the effect of different acids on their absorption would also be similar. Initial experiments showed that the atomic absorption of some of them was sensitive to the type of acid used. An investigation was undertaken to study the effect of various acids on the atomic absorption of rare earths. The acids used were hydrochloric, sulphuric, nitric and perchloric, and the elements investigated were yttrium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium. The purpose of this paper is to present some of the pertinent results of this investigation.

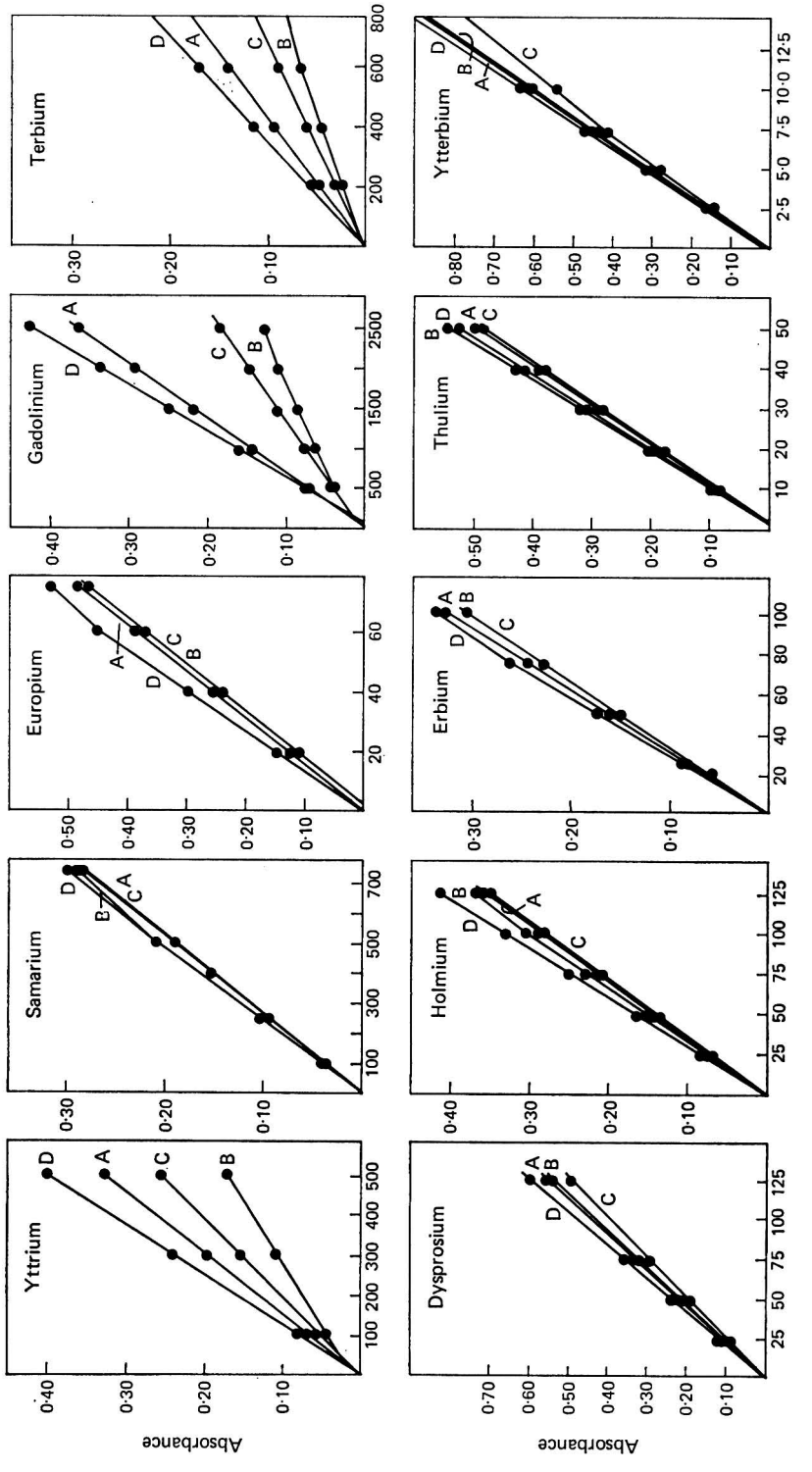

Fig. 1. Effect of various acids on the absorbance of rare earths. Curves A, 0·5 M hydrochloric acid; curves B, 0·5 M sulphuric acid; curves C, 0·5 M nitric acid; and curves D, 0·5 M perchloric acid

Experimental

Apparatus—

A Techtron, Model AA-3, flame spectrophotometer fitted with an AA-4 gas control unit and an AA-5 atomiser - burner assembly with a nitrous oxide - acetylene burner head was used.

Experimental conditions—

The analytical lines used were yttrium 410·2 nm, samarium 429·6 nm, europium 459·4 nm, gadolinium 368·4 nm, terbium 432·6 nm, dysprosium 421·1 nm, holmium 410·3 nm, erbium 400·8 nm, thulium 371·8 nm and ytterbium 398·8 nm. The nitrous oxide pressure was 20 p.s.i. Acetylene flow-rate, lamp current, burner elevation, slit width and aspiration rate were adjusted for each element to obtain optimum absorption readings with minimum noise levels. The optimisation of the instrument was achieved with solutions of the rare earths in hydrochloric acid media and no further adjustment was made for solutions containing other acids.

Reagents and solutions—

The rare earths were either 99·9 or 99·99 per cent. pure oxides. All other reagents were of analytical-reagent grade. Standard stock solutions were prepared to contain 10 000 p.p.m. of gadolinium, 4000 p.p.m. of yttrium, samarium and terbium, 1000 p.p.m. of dysprosium and holmium, 400 p.p.m. of europium and erbium, 200 p.p.m. of thulium and 100 p.p.m. of ytterbium by separately dissolving appropriate amounts of the rare-earth oxides in a slight excess of 6 M hydrochloric acid and diluting to volume with deionised water. To determine the effect of different acids, sets of standard solutions were prepared from the stock solutions, and hydrochloric, sulphuric, nitric and perchloric acids were added separately to give 0·5 M acid concentrations. The sets of solutions prepared contained 100 to 500 p.p.m. of yttrium, 100 to 750 p.p.m. of samarium, 20 to 75 p.p.m. of europium, 500 to 2500 p.p.m. of gadolinium, 200 to 800 p.p.m. of terbium, 25 to 125 p.p.m. of dysprosium, 25 to 125 p.p.m. of holmium, 20 to 100 p.p.m. of erbium, 10 to 50 p.p.m. of thulium and 1 to 20 p.p.m. of ytterbium. To determine the effect of increasing acid concentration, sets of solutions, each containing the same amounts of rare earths, were prepared from the stock solutions, and hydrochloric, sulphuric, nitric and perchloric acids were separately added in increasing amounts to these solutions. To determine the effect of enhancing agents, potassium chloride was added to the above solutions at a concentration of 1000 p.p.m.

Results

Effect of various acids—

Fig. 1 shows the absorbance as a function of concentration for yttrium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium in 0·5 M hydrochloric acid (curves A), in 0·5 M sulphuric acid (curves B), in 0·5 M nitric acid (curves C) and in 0·5 M perchloric acid (curves D). From these curves the rare earths can be categorised into two groups according to their absorption behaviour in different acids. The elements in group I are samarium, europium, dysprosium, holmium, erbium, thulium and ytterbium, and the absorbance - concentration curves of these elements varied only slightly with the type of acid used. Those in group II are yttrium, gadolinium and terbium, which showed great sensitivity to the type of acid used. The highest absorption was obtained in perchloric acid and the lowest in sulphuric acid. The degree of absorption increased in the following order of acids: sulphuric, nitric, hydrochloric and perchloric.

Effect of acid concentration—

Fig. 2 shows the absorbance as a function of acid concentration for 30 p.p.m. of thulium. The curves are typical of the elements in group I. It is evident that when the acid concentration was in the range 0·1 to 0·5 M the absorption was not affected by the acid concentration. When the acid concentration was increased from 0·5 to 3·0 M, however, the absorption decreased gradually for hydrochloric acid (curve A) and perchloric acid (curve D). For sulphuric acid (curve B) the absorption decreased significantly. On the other hand, the absorption remained essentially unchanged for nitric acid (curve C).

The elements in group II showed a similar effect to those in group I in 0·1 to 3·0 M hydrochloric and perchloric acid media (curves not shown). The effect of sulphuric and

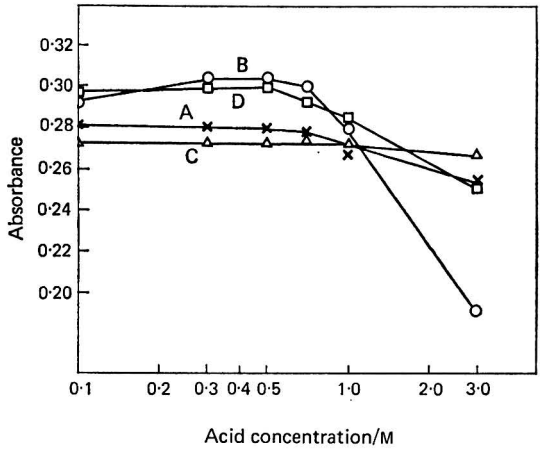

Fig. 2. Effect of increasing acid concentration on the absorbance of 30 μg ml^{-1} of thulium. Curve A, hydrochloric acid; curve B, sulphuric acid; curve C, nitric acid; and curve D, perchloric acid

nitric acids was determined for concentrations between 0·001 and 3·0 M because these acids showed the greatest suppression. Fig. 3 shows the absorbance as a function of sulphuric acid (curve A_1) and nitric acid (curve B_1) concentrations for 400 p.p.m. of yttrium. Gadolinium and terbium gave similar curves. As the acid concentration increased from 0·001 to 0·10 M the absorption decreased rapidly to a minimum, which is about equal to the amount of nitrate or sulphate required to form yttrium sulphate or nitrate. The absorption then increased with concentration up to 0·5 M and remained constant up to 3·0 M concentration. Because of the effect of sulphate and nitrate at low concentrations, these anions should be eliminated when the elements in group II are determined.

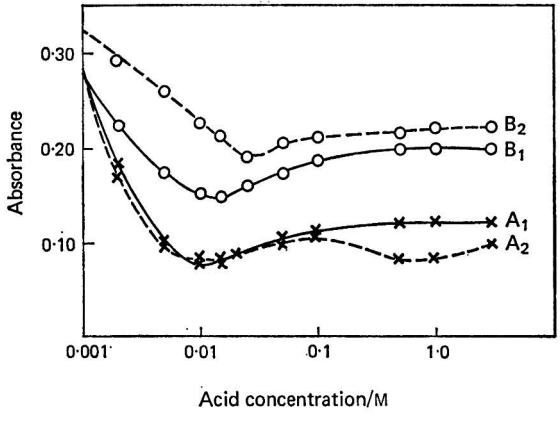

Fig. 3. Effect of increasing acid concentration on the absorbance of 400 μg ml^{-1} of yttrium with and without enhancing agent. Curve A_1, sulphuric acid; curve B_1, nitric acid; curve A_2, sulphuric acid *plus* 1000 μg ml^{-1} of potassium chloride; curve B_2, nitric acid *plus* 1000 μg ml^{-1} of potassium chloride

EFFECT OF ENHANCING AGENTS—

Enhancing agents such as potassium chloride, ammonium chloride, EDTA and strontium chloride are often used to increase the number of ground-state atoms in the flame. In Fig. 3, curves A_2 and B_2 show the effect of 1000 p.p.m. of potassium chloride on the absorbance of 400 p.p.m. of yttrium in sulphuric and nitric acid media, respectively, when the acid concentrations were increased from 0·001 to 3·0 M. In nitric acid the addition of potassium chloride increased the absorption, but the shape of the curve is similar to that without enhancing agent (curve B_1). In sulphuric acid of concentration up to 0·10 M the addition of potassium chloride did not change the absorbance of yttrium, but caused a decrease in the absorbance at higher acid concentrations. Various other enhancing agents, some of them at concentrations of several thousand parts per million, were also tried, but none released the suppression caused by the sulphuric acid.

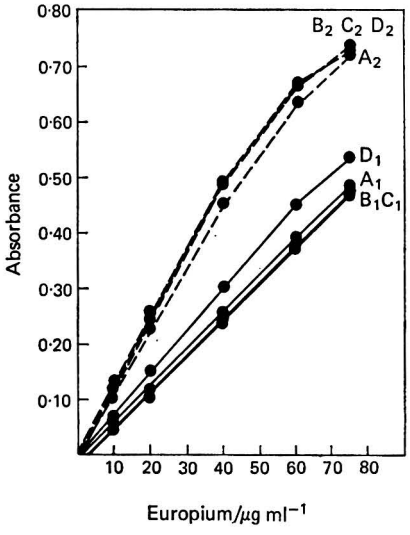

Fig. 4. Effect of 1000 μg ml^{-1} of potassium chloride on the absorbance of europium in various acidic media. Curve A_2, 0·5 M hydrochloric acid; curve B_2, 0·5 M sulphuric acid; curve C_2, 0·5 M nitric acid; and curve D_2, 0·5 M perchloric acid. Curves A_1 to D_1 are the same absorbance curves as A_2 to D_2 without potassium chloride

The effect of 1000 p.p.m. of potassium chloride on the absorbance of europium in 0·5 M hydrochloric, sulphuric, nitric and perchloric acid media (curves A_2 to D_2) is shown in Fig. 4. Curves A_1 to D_1 show the absorbance of the same europium solutions without enhancing agents. These curves are typical of elements in group I. It can be seen that the addition of potassium chloride increased the absorption in a similar way for all the acids. When potassium chloride was added to solutions containing perchloric acid, however, salt formation occurred in the burner slit. This salt build-up necessitated the frequent cleaning of the burner and made the determination slow. Therefore, although the addition of potassium chloride increased the absorption of europium or group I rare earths, its use is not recommended in perchloric acid media.

The effect of potassium chloride on the absorbance of gadolinium in 0·5 M hydrochloric, sulphuric, nitric and perchloric acid media (curves A_2 to D_2) is shown in Fig. 5. Curves A_1 to D_1 are the absorbance curves of the same gadolinium solutions without enhancing

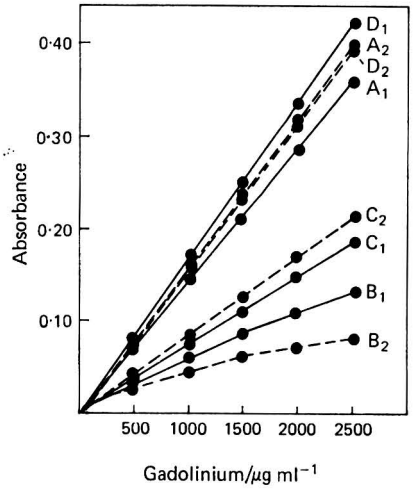

Fig. 5. Effect of 1000 μg ml^{-1} of potassium chloride on the absorbance of gadolinium in various acidic media. Curve A_2, 0·5 M hydrochloric acid; curve B_2, 0·5 M sulphuric acid; curve C_2, 0·5 M nitric acid; and curve D_2, 0·5 M perchloric acid. Curves A_1 to D_1 are the same absorbance curves as A_2 to D_2 without potassium chloride

agents. These curves are typical of the elements in group II. The addition of potassium chloride increased the absorption slightly in hydrochloric and nitric acids, decreased it slightly in perchloric acid and decreased it greatly in sulphuric acid media.

Discussion

The rare earths were categorised into two groups according to their behaviour in various acids. The elements in group I showed little change in absorption in the four acids. The elements in group II showed great sensitivity to the type of acid used. The atomic absorption of any element depends on the number of ground-state atoms formed in the flame. The ground-state atom formation is governed by the process of solvent evaporation, vaporisation of solid particles and the dissociation of the gaseous compounds to atoms.[5] The behaviour of group II elements can be explained by the higher dissociation energies of compounds containing rare earth ions with more stable electronic configurations. The ions from samarium to ytterbium all have incomplete 4f electron shells, whereas yttrium(III) has an electronic structure of $4s^24p^6$, which is a very stable structure. It is known that within the group of rare earth ions there are three electronic configurations that lead to the formation of stable ions.[6,7] The first and most stable of these is lanthanum(III) with no 4f electrons, the second is gadolinium(III) with a half-filled 4f shell ($4f^7$) and then lutetium(III) with a completely filled 4f shell. The behaviour of terbium can be explained by the formation of terbium(IV) compounds in the flame, which lead to a stable electronic configuration of the gadolinium(III) type. Consequently, one can expect that lanthanum and lutetium will show absorption behaviour similar to that shown by yttrium, gadolinium and terbium. Europium and ytterbium in the bivalent state have stable electronic configurations similar to those of gadolinium(III) and lutetium(III), respectively. These dipositive ions, however, are strong reducing agents and are readily oxidised to the trivalent state, and therefore behave in a similar way to group I elements.

As shown above, elements in group II have a more stable ionic structure than those in group I, and consequently require more energy to form atoms in the flame. The energy of the high-temperature nitrous oxide - acetylene flame is sufficient to produce enough

ground-state atoms from the chloride compounds to obtain absorbance - concentration curves of analytical use. It seems that the nitrate compounds decompose more readily to oxides, which are not so easily atomised. The addition of potassium chloride increased the number of rare earth atoms in the flame in nitric acid but not sufficiently to provide useful analytical media. The effect of sulphuric acid is slightly different. No release of suppression was achieved with enhancing agents, which could indicate that the rare earths may be present in the flame in the form of sulphate, and that the short residence time is not sufficient to decompose them to oxides. However, at present there is not enough evidence to substantiate this theory.

Conclusion

The rare earths investigated can be separated into two groups according to their behaviour in hydrochloric, sulphuric, nitric and perchloric acid media. Elements in group I can be determined in all four acids in the concentration range 0·1 to 0·5 M. Those in group II can be determined in hydrochloric or perchloric acid in the concentration range 0·1 to 0·5 M. Any sulphate or nitrate present in the original sample should be removed when elements in group II are determined. The addition of potassium chloride enhanced the absorption of the rare earths but is not recommended in perchloric acid media.

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High Precision Spectrophotometry

Part I. Assessment of the Performance of the Unicam SP3000 Spectrophotometer and its Application to the Determination of Phosphate in Fertilisers and Related Materials

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By using conventional, single-beam spectrophotometers the ultimate precision that can be achieved by direct absorbance measurements is about 0·5 per cent. relative. Greater precision can be obtained if measurements are made differentially. Recently, more advanced spectrophotometers have become available that enable measurements to be carried out directly with a precision comparable with that obtained by use of differential techniques. In this paper the performance of such an instrument, the Unicam SP3000, is discussed and its application to the precise determination of phosphate in fertilisers and intermediates is described.

SPECTROPHOTOMETRIC methods of analysis in the early years following the advent of commercial photoelectric spectrophotometers were, because of the lack of precision associated with the technique, usually restricted to the determination of minor constituents. For the determination of major constituents classical gravimetric and titrimetric techniques were preferred even though they made greater demands on the time and skill of the analyst. The determination of major amounts of copper in copper-base alloys, described by Bastian[1] in 1949, was the first practical application of differential spectrophotometry to be reported. This technique, which combines greater precision with the advantages of speed and simplicity inherent in photometric methods, has, since that time, found extensive use in the determination of high percentages of numerous elements.[2] However, when large numbers of photometric measurements are made differentially, the operations of cell handling, setting of instrument controls and scale reading involved prove rather monotonous. The Unicam SP3000 system was designed to eliminate these operations and to provide a means by which spectrophotometric measurements could be made directly against pure solvent with a precision comparable with that obtained with differential techniques.

This paper describes experimental work designed to evaluate some of the claims made for the instrument. The assessment covered those aspects of instrument performance that are pertinent to certain types of spectrophotometric analysis in use in our laboratories. For example, in multi-component analysis in the ultraviolet region of the spectrum[3] the calibration of the spectrophotometer is usually a lengthy procedure, and in an industrial laboratory it is not always practical for a calibration to be run with each batch of samples examined. Frequent calibration of the instrument can be avoided if it is established that the wavelength and photometric repeatability of the spectrophotometer are of a high order. Examination of the Unicam SP3000 in relation to these two parameters forms the substance of the first section of this paper.

Because phosphate is an important major constituent of raw materials, intermediates and finished products in the fertiliser industry, its determination is also of particular interest. Considerable attention has been paid in the past to its accurate determination[4–13] and there exist a number of recognised standard procedures for the determination of phosphate in such matrices. It was therefore considered appropriate to compare the existing titrimetric and differential spectrophotometric procedures[14] with a direct spectrophotometric procedure involving the Unicam SP3000.

Experimental

Apparatus—

The complete Unicam SP3000 system is described in the manufacturer's literature and elsewhere.[15,16] The accessories used in conjunction with the basic instrument were the Unicam SP3001 automatic digital printer and the Unicam SP3007 constant-temperature cell holder. The temperature of the block of the cell holder was maintained constant by water circulating from a Churchill laboratory thermo-circulator.*

Assessment of instrument performance—

(*a*) *Wavelength accuracy and repeatability*—Regular checks over a period of 1 year on the wavelength calibration of the instrument in both the ultraviolet and visible light regions have been made by location of the characteristic absorption peaks of holmium glass (Chance ON12) and didymium glass (Corning 3130) filters. The results obtained are summarised in Table I. They indicate that the accuracy of the wavelength calibration is within the tolerances given in the manufacturer's specification. The repeatability of the wavelength calibration is extremely good; indeed, the greatest deviation from mean peak wavelength values in the ultraviolet region of the spectrum did not exceed 0·2 nm. A wavelength variation of this magnitude would result in serious errors only if measurements were made in regions of spectra where absorbance changed extremely rapidly with increase or decrease in wavelength.

Table I

Accuracy and repeatability of wavelength selection

Filter		Holmium									Didymium		
Wavelength of absorption peak/nm		241·5	279·4	287·5	333·7	360·5	418·4	453·2	536·2	637·5	573	586	685
Mean wavelength observed/nm		241·3	279·4	287·6	333·9	360·5	418·4	453·2	536·5	639·0	573	585	685
Maximum deviation from mean/nm	+	0·2	0·1	0·2	0·2	0·2	0·1	0·3	0·5	1·0	1	1	1
	−	0	0·2	0·1	0·1	0·2	0·2	0·4	0·5	1·0	0	1	1

(*b*) *Short-term photometric repeatability*—A series of solutions of analytical-reagent grade potassium dichromate at various concentration levels in 0·01 N sulphuric acid were prepared. The absorbance of each solution, at the wavelength of minimum absorbance (235 nm), was measured thirty-six times against distilled water in silica cells with a 1-cm light path, the sample cell being filled with a fresh portion of the test solution before each measurement. The entire series of measurements was completed within a period of 3 hours.

A second series of more concentrated dichromate solutions was prepared and on this occasion absorbance measurements were made at 420 nm. The standard deviation of each set of thirty-six measurements at each wavelength was calculated and the values obtained are shown in Table II.

Table II

Reproducibility of absorbance measurements on potassium dichromate solutions at various concentration levels

Mean absorbance (36 measurements) at a wavelength of		Standard deviation × 10^5 at a wavelength of	
235 nm	420 nm	235 nm	420 nm
—	0·2175	—	61
0·2523	—	45	—
0·2907	—	68	—
—	0·4434	—	65
0·5328	—	52	—
—	0·6755	—	61
0·7409	—	49	—
0·8843	—	47	—
—	0·9067	—	67
0·9915	—	70	—
1·1371	—	47	—

* Supplied by the Churchill Instrument Co. Ltd., Perivale, Greenford, Middlesex.

From these results it is apparent that the reproducibility of absorbance measurements is independent of the absorbance value over the range covered and is better than the read-out resolution of the instrument (±0·001 absorbance unit). It can be concluded, therefore, that the relative error of absorbance measurement is least at the higher absorbance values. This relationship between photometric precision and absorbance level is in contrast to that which obtains with conventional instruments as with these the minimum relative error is generally considered to occur at an absorbance of 0·434.

(*c*) *Long-term photometric repeatability*—A dichromate solution, having an absorbance (at a wavelength of 235 nm) in the range where the photometric accuracy of the instrument is claimed to be optimum (*i.e.*, "near to 0·800"),[15] was prepared by dissolving 140 mg of analytical-reagent grade potassium dichromate in 2 litres of 0·01 N sulphuric acid. This solution was stored in an air-tight glass bottle that had been degreased and cleaned with ethanolic potassium hydroxide solution, then thoroughly washed with distilled water and rinsed with small volumes of the prepared dichromate solution.

At intervals, over a period of 5 months, the absorbance of this solution at a temperature of 25 °C and wavelength of 235 nm was measured against distilled water in 1-cm light path silica cells. Triplicate measurements were made on each occasion, the sample being transferred directly from the storage bottle to the measuring cell by means of the Autocell sampling device. The sample cell was emptied, then filled with a fresh portion of the test solution before each measurement. A graph in which the mean of each set of triplicate absorbance values is plotted against the age of the solution is shown in Fig. 1. It is evident that the apparent absorbance varies randomly with time, the difference between the highest and lowest values recorded being 0·008. Such a random variation is unlikely to be attributable to a solution variable, especially as the temperature was rigidly controlled. The standard deviation of the results shown in Fig. 1 is 0·0022 whereas that for short-term repeatability, calculated by pooling the data furnished by each set of triplicate measurements, is 0·0005.

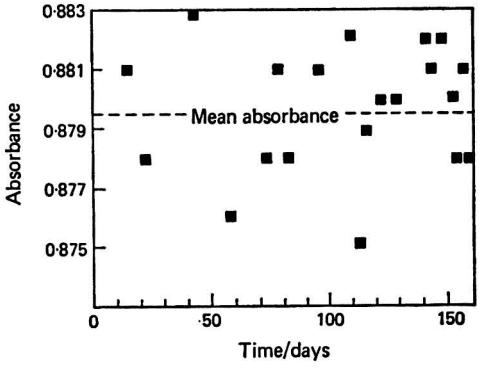

Fig. 1. Long-term repeatability of absorbance measurement of a standard dichromate solution. Absorbance of a 1-cm layer at a wavelength of 235 nm

It was suggested by the manufacturer that the long-term repeatability might be improved by daily adjustment of "zero per cent. transmittance" (dark current) instead of monthly, as recommended in the operating manual. A further long-term repeatability test was therefore made, the dark current being checked before each set of triplicate measurements. There was no improvement in the repeatability of the results.

The disparity between the long and short-term repeatability implies that when results of extremely high accuracy are required it is essential that the time interval between calibration of the instrument and measurement of the sample solution is limited to as short a period as possible.

Determination of phosphate

Phosphoric acid liquors: comparison of a titrimetric procedure with a direct spectrophotometric procedure—

The titrimetric method, based on precipitation of phosphate as quinolinium molybdophosphate,[5,6] has been extensively used for the routine determination of phosphate in phosphoric acid liquors. A spectrophotometric procedure based on direct measurement of the intensity of the orange - yellow coloured molybdovanadophosphoric acid[4] is available, but when a conventional spectrophotometer is used the results obtained are not sufficiently precise for the determination of phosphate in concentrated phosphoric acid liquors.

A series of phosphoric acid liquors was examined, under routine conditions, for phosphate content. Catch weights of each sample were diluted to provide working solutions containing between 3 and 5 g of phosphorus pentoxide per litre. The phosphate concentration of each of these working solutions was determined by the titrimetric procedure and by a direct spectrophotometric procedure, absorbance measurements being made with the Unicam SP3000. Statistical treatment of the results shown in Table III revealed that, under the test conditions, there is no significant bias towards either of the two procedures and also that the spectrophotometric procedure is more precise than the titrimetric procedure. The coefficient of variation calculated from the eleven sets of duplicate spectrophotometric determinations is 0·2 per cent., while that for the sixteen sets of duplicate titrimetric determinations is 0·5 per cent.

Table III

Comparison of results for the determination of phosphate in phosphoric acid liquors by the titrimetric and direct spectrophotometric procedures

Sample number	Phosphorus pentoxide, per cent. w/w: Titrimetric method		Phosphorus pentoxide, per cent. w/w: Spectrophotometric method		Sample number	Phosphorus pentoxide, per cent. w/w: Titrimetric method		Phosphorus pentoxide, per cent. w/w: Spectrophotometric method	
1	45·0	45·6	45·5	45·3	12	29·2	29·7	29·6	
2	45·9	45·9	46·2	46·1	13	29·8	29·7	29·5	
3	42·7	42·8	42·9		14	13·5		13·4	13·4
4	43·8	43·5	43·8		15	37·9	37·8	37·5	37·7
5	38·5	38·7	39·0		16	26·5	26·6	26·3	26·4
6	40·9	40·5	41·3		17	13·0		12·9	12·9
7	42·2	41·8	41·9		18	37·9		37·8	37·8
8	42·7	42·5	42·8		19	42·8		42·8	42·8
9	44·7	44·6	44·6		20	43·5	42·9	42·6	42·5
10	41·8	41·6	41·4		21	42·5		42·6	42·6
11	43·4	43·1	43·2		22	43·6		43·7	43·8

Average difference between results obtained by direct spectrophotometric procedure and results obtained by titrimetric procedure is +0·005 per cent.

Fertilisers: comparison of differential and direct spectrophotometric procedures—

The spectrophotometric vanadate - molybdate procedure for the determination of phosphate as described in the Fertilizers and Feeding Stuffs Regulations[14] requires the use of a form of differential measurement, namely, the transmittance ratio method. In this technique light transmitted by a sample solution in one of a pair of matched 1-cm light path cells is measured against the light transmitted by a solution of known phosphate concentration in the other cell. A series of seven fertilisers was used in a comparison of the precision obtainable with this measuring technique against that with direct measurement of the sample solution against water in a Unicam SP3000. Replicate solutions of the molybdovanadophosphate complex were prepared, each from a separate sample weight of the fertiliser. These solutions were measured, at a wavelength of 425 nm, in a Unicam SP600 spectrophotometer against a standard molybdovanadophosphoric acid solution containing 5·00 mg of phosphorus pentoxide per 100 ml, and then, at the same wavelength, against water in the

Unicam SP3000. The phosphate concentration of each fertiliser was calculated by reference to appropriate calibrations prepared for each instrument by using a set of standard molybdovanadophosphoric acid solutions covering the range from 5·00 to 6·00 mg of phosphorus pentoxide. The results are shown in Table IV.

TABLE IV

COMPARISON OF RESULTS FOR THE DETERMINATION OF PHOSPHATE IN FERTILISERS BY THE DIRECT AND DIFFERENTIAL SPECTROPHOTOMETRIC PROCEDURES

		Phosphorus pentoxide, per cent. w/w			
		Direct method (SP3000)		Differential method (SP600)	
Fertiliser	Test number	Determined	Mean value	Determined	Mean value
A	1	8·87		8·86	
	2	8·91		8·86	
	3	8·93	8·89	8·87	8·87
	4	8·86		8·85	
	5	8·89		8·90	
B	1	17·27		17·31	
	2	17·20		17·26	
	3	17·27	17·22	17·26	17·27
	4	17·18		17·24	
	5	17·18		17·27	
C	1	20·50		20·47	
	2	20·51		20·53	
	3	20·52	20·52	20·46	20·49
	4	20·54		20·50	
	5	20·52		20·50	
D	1	24·09		24·18	
	2	24·00		24·11	
	3	24·18	24·11	24·23	24·19
	4	24·07		24·16	
	5	24·20		24·26	
E	1	9·31		9·30	
	2	9·33		9·33	
	3	9·33	9·32	9·33	9·32
	4	9·32		9·33	
	5	9·32		9·31	
F	1	13·31		13·24	
	2	13·32		13·27	
	3	13·31	13·31	13·26	13·26
	4	13·32		13·27	
	5	13·31		13·24	
G	1	11·39		11·46	
	2	11·40	11·40	11·45	11·46
	3	11·41		11·48	
	4	11·39		11·46	

The coefficient of variation calculated for the thirty-four results from the differential method is 0·20 per cent. whereas that for the thirty-four results from the direct method with use of the Unicam SP3000 is 0·27 per cent. The time taken for a measurement on the Unicam SP3000 is 28 s against the 2½ minutes required for the Unicam SP600.

CONCLUSION

In the assessment of the performance of the Unicam SP3000 it has been shown that the accuracy of the wavelength calibration is within the limits given by the manufacturer and that the wavelength repeatability is extremely good. It has been established that the short-term photometric repeatability of absorbance measurement is independent of the absorbance value over the range from 0 to 1·2 absorbance units and is better than the read-out resolution (0·001 absorbance unit). The reason for the somewhat erratic results observed in the long-term photometric repeatability tests remains obscure. A more extensive series of tests in which two absorbing systems and a second ultraviolet spectrophotometer are used might help to reveal the source of the variations observed.

For routine determinations of phosphate in phosphoric acid liquors the direct spectrophotometric molybdovanadophosphoric acid method is more precise than the titrimetric quinolinium molybdophosphate procedure. Further, with the spectrophotometric method there is a considerable saving of time.

The comparison of the differential and direct spectrophotometric procedures for the precise determination of phosphate showed that the direct procedure with the Unicam SP3000 did not appear to offer a significant improvement in precision over that obtained by use of the differential technique with a Unicam SP600. Nevertheless, there is a considerable reduction in instrument time and fewer demands are made on the operator. From this point of view alone there is a significant advantage in the use of the Unicam SP3000 when dealing with large numbers of samples.

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NOTE—Reference 3 is to Part II of this series.

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High Precision Spectrophotometry

Part II. The Determination of Ammelide, Ammeline and Melamine in the Thermal Decomposition Products of Urea

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An automatic ultraviolet spectrophotometric method is described for the determination of ammelide, ammeline and melamine in the thermal decomposition products of urea; prior separation of the components is unnecessary. A Unicam SP3000 spectrophotometer is used to make absorbance measurements at several different wavelengths and at two pH values. From the absorbance values obtained the concentrations of the amino-*s*-triazines are calculated by using a computer to solve the appropriate simultaneous equations. The constants required in these equations are obtained by calibration of the spectrophotometer with solutions of the pure compounds. A semi-quantitative estimation of triuret is also possible. Interferences caused by biuret and cyanuric acid can normally be ignored, but corrections are required if large amounts are present.

IN Part I an assessment of the performance of the Unicam SP3000 spectrophotometer was made and its use in the determination of phosphate in fertilisers and related materials was reported.[1] The work described in the present paper relates to the application of the instrument to the development of a rapid ultraviolet method for the simultaneous determination of the three amino-*s*-triazines ammelide, ammeline and melamine in the thermal decomposition products of urea. The Unicam SP3000 system is particularly suitable for this type of work because of the availability of an automatic wavelength selector as an accessory (SP3003),[2] which permits absorbance measurements to be made on each sample solution at up to five accurately pre-set wavelengths, its good long and short-term photometric repeatability[1] and its automatic cell filling device, which eliminates absorbance errors caused by cell handling.

Various authors[3–6] have described procedures for the determination of the amino-*s*-triazines that involve laborious multiple separations based on the different solubilities of the compounds and their salts. In other methods separation by ion-exchange chromatography followed by ultraviolet spectrophotometric measurement has been proposed.[7,8] However, even the fastest of these chromatographic separations requires several hours for completion. Boitsov and Finkel'shtein[9] have described a more rapid procedure for the determination of cyanuric acid, ammelide, ammeline and melamine in the hydrolysis products of melamine. In their method absorbance measurements are made on a solution of the sample in 0·05 M borax solution at wavelengths of 216 and 231·5 nm and in 0·1 N hydrochloric acid at 215 and 230 nm. The concentration of each component is calculated by solving four simultaneous equations set up by calibration of the spectrophotometer with solutions of the pure compounds. This method is not generally applicable to the analysis of urea pyrolysates because of the presence of other products such as biuret and triuret, which absorb strongly in an alkaline medium at 216 nm.

In developing a method of multi-component spectrophotometric analysis it is important to select conditions such that the absorbance of each compound to be determined is large compared with the background absorbance due to contributions from other species. Of the compounds that occur in urea pyrolysates, the following are known to absorb in the 200 to 240-nm wavelength ultraviolet region: biuret, triuret, cyanuric acid, ammelide, ammeline, melamine, melam and melem. The last two components are formed at temperatures well above the range required for optimum yields of products of commercial interest. Of the other compounds mentioned, the three amino-*s*-triazines alone exhibit strong absorption bands in acidic solution in the region of interest. It seemed, therefore, that it would be best to attempt to determine the amino-*s*-triazines in acidic solution so that interference from other compounds would be minimised.

Experimental

Purification of compounds used as standards—

Urea and melamine of very high purity are commercially available; Aristar grade urea and Organic Analytical Standard grade melamine (B.D.H. Ltd.) were used.

Laboratory-reagent grade biuret was recrystallised twice from ethanol after removal of cyanurate with an anion-exchange resin. The product was dried at 85 °C.

Pure triuret (melting-point 231 °C) was prepared by the reaction of urea with thionyl chloride, as described by Haworth and Mann.[10]

Laboratory-reagent grade cyanuric acid was recrystallised twice from water and then dried at 105 °C.

Crude ammelide, containing a significant amount of ammeline and small amounts of other decomposition products of urea, was purified by a technique based on a separation procedure described by Bieling and Laabs.[11] The impure ammelide (40 g) was dissolved in 2 litres of a hot, 5 per cent. w/v sodium carbonate solution. After cooling and standing overnight the insoluble material (mainly ammeline) was filtered off. Ammelide in the filtrate was precipitated following neutralisation with acetic acid. After filtration, the solid product was dissolved in more hot sodium carbonate solution and the purification procedure was repeated twice. The final product was thoroughly washed with water, then dried at 105 °C. The nitrogen content of the dried material was determined and found to be 43·5 per cent. [the calculated nitrogen content of ammelide ($C_3H_4N_4O_2$) being 43·7 per cent.].

Ammeline was prepared by the reaction of urea with dicyandiamide. The product, contaminated with ammelide and melamine, was purified by preparative scale anion-exchange chromatography based on an analytical procedure of Bacaloglu, Csunderlik and Ostragovich.[8] The alkaline fraction containing the ammeline was neutralised with hydrochloric acid and the precipitate filtered off, then re-dissolved in sodium hydroxide solution. The fractionation and precipitation stages were then repeated. The solid product was washed with water until free from acid and then dried at 105 °C. The nitrogen content of the dried material was determined and found to be 55·0 per cent. [the calculated nitrogen content of ammeline ($C_3H_5N_5O$) being 55·1 per cent.].

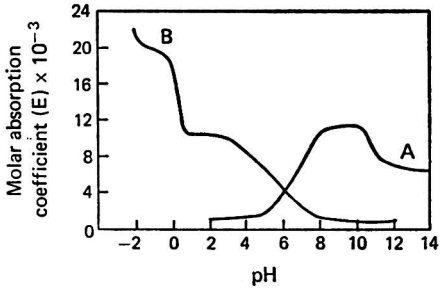

Fig. 1. Molar absorption coefficients of cyanuric acid and melamine at various pH values (reference 13): A, cyanuric acid (λ=220 nm); and B, melamine (λ=236 nm)

Influence of pH on the absorbance of ammelide, ammeline and melamine—

Hirt and Schmitt[12] and Boitsov and Finkel'shtein[13] have carried out detailed investigations into the variation of the molar absorption coefficients of ammelide, ammeline, melamine and cyanuric acid as a function of the pH of the medium. Figs. 1 and 2 are reproduced from Boitsov and Finkel'shtein's paper. Minimum slopes in each curve represent regions where a single ionic or molecular species exists; elsewhere an acid and its conjugate base possessing different absorption coefficients are in equilibrium. It is apparent that at about pH 0 the absorbance of ammelide is too low to be of use in the determination of this compound; further, between pH 3·5 and pH 6, where the absorbance of ammelide is high and stable,

the absorbances of ammeline and melamine decrease quite abruptly with increasing pH. This relationship is reversed in the pH range from 0 to 3·5, as here the absorbances of ammeline and melamine are fairly constant but that of ammelide increases rapidly with pH. Thus it is evident that if an acidic medium is to be used in the three-component determination of the amino-*s*-triazines it must have a high level of isoprotic efficiency to minimise absorbance errors that could arise from variations in the acidity or alkalinity of urea pyrolysates.

It was decided to work at two pH levels, one at approximately pH 3, where ammelide has a large absorbance, and the other at about pH 0, where ammeline and melamine can be examined in virtual isolation from ammelide, which has a very low absorbance at this pH.

Because ammelide and ammeline were found to be more soluble, and less susceptible to hydrolysis, in alkalis than acids, samples and standards were dissolved in sodium hydroxide solution. A 25-ml volume of 0·2 M hydrochloric acid - 1·0 M potassium dihydrogen phosphate buffer solution proved suitable for the control of final solutions (100 ml) at pH 3. Separate final solutions adjusted to 1·95 N with respect to hydrochloric acid were prepared for measurements at a pH just below zero. The absorbances of the reagent blanks prepared in either manner were less than 0·07 absorbance unit in the wavelength region concerned.

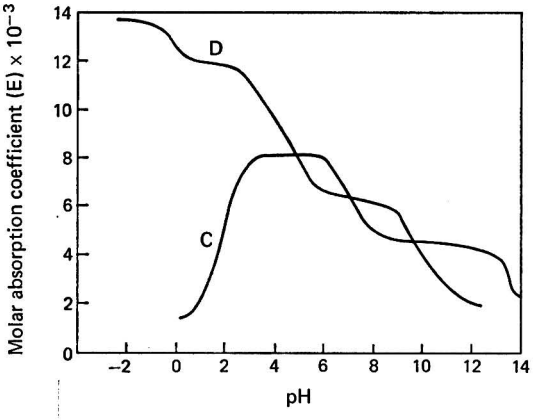

Fig. 2. Molar absorption coefficients of ammelide and ammeline at various pH values (reference 13): C, ammelide (λ=226 nm); and D, ammeline (λ=230 nm)

Choice of analytical wavelengths—

The absorption spectra of ammelide, ammeline and melamine at a concentration of 1 mg per 100 ml in phosphate buffer at pH 3 and in 1·95 N hydrochloric acid were recorded on a Unicam SP800 and are shown in Figs. 3 and 4, respectively. At pH 3 there is considerable overlapping of the absorption curves of the three compounds. The analytical wavelength chosen for ammelide was 221 nm because at this wavelength the ratios of the absorption coefficient of this compound to the absorption coefficients of the other two compounds are at a maximum. The wavelength maximum at 229 nm in the more strongly acidic solution was adopted as the analytical wavelength for ammeline for the same reason. The wavelength initially chosen for melamine was 236 nm in 1·95 N hydrochloric acid; however, measurements are now made at 240 nm, where the overlap of the melamine curve by that of ammeline is less severe. Although in this region the absorbance changes fairly rapidly with wavelength, experience with the instrument has shown that the wavelength settings can be made with a high degree of precision and serious errors do not result from operating in such a region.

Effect of temperature on the absorbances of ammelide, ammeline and melamine—

A solution of 1 mg of ammelide in 100 ml of phosphate buffer was introduced into a 1-cm light path silica cell housed in the SP3007 constant-temperature cell holder. The temperature of the water circulating through the cell-holder block was slowly raised from

20 to 35 °C. The absorbance of the ammelide solution at a wavelength of 221 nm against a blank increased at the rate of 0·0024 absorbance unit per °C. In similar experiments the absorbance at 229 nm of 0·5 mg of ammeline in 100 ml of 1·95 N hydrochloric acid was found to decrease by 0·0007 absorbance unit per °C, whereas the absorbance at 240 nm of 1 mg of melamine in 100 ml of 1·95 N hydrochloric acid increased, but by less than 0·0003 absorption unit per °C. As a result of these findings it was decided that final solutions should be measured at 25 ± 0·5 °C.

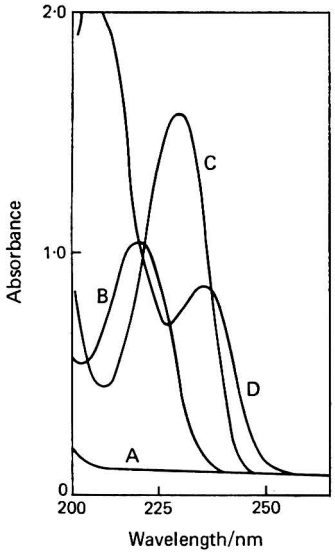

Fig. 3. Absorption spectra of ammelide, ammeline and melamine in phosphate buffer (pH 3): A, blank; B, ammelide (1mg per 100 ml); C, ammeline (1mg per 100ml); and D, melamine (1mg per 100ml)

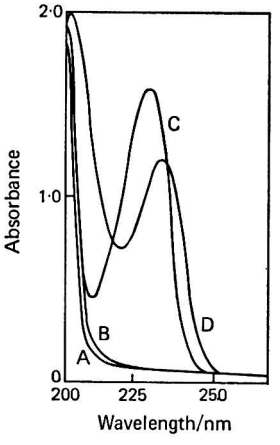

Fig. 4. Absorption spectra of ammelide, ammeline and melamine in acidic solution (1·95 N HCl, about pH 0): A, blank; B, ammelide (1mg per 100ml); C, ammeline (1mg per 100ml); and D, melamine (1mg per 100ml)

ADDITIVITY OF ABSORBANCES OF AMMELIDE, AMMELINE AND MELAMINE—

Although linear relationships between concentration and absorbance for solutions of ammelide, ammeline and melamine in acidic media have been reported in the literature[8,9] this was verified for the pure compounds in phosphate buffer solution and 1·95 N hydrochloric acid. Essentially linear calibrations were found over the concentration range from 0 to 1 mg per 100 ml of each compound in phosphate buffer at a wavelength of 221 nm: for 0 to 5 mg of ammelide, 0 to 0·5 mg of ammeline and 0 to 1 mg of melamine per 100 ml of acid at 229 nm, and for 0 to 5 mg of ammelide and 0 to 1 mg of ammeline and melamine per 100 ml of acid at 240 nm. On the basis of these absorbance measurements a set of absorption coefficients (absorbance of 1 mg of the compound per 100 ml of final solution) was calculated.

If it is assumed that the absorbances of the three compounds at each wavelength are additive, then the relationships between the absorbances of a mixture of the compounds and the concentrations of the individual components can be expressed by three simultaneous equations [equations (1), (2) and (3) under Calculation]. To establish the validity of these equations a series of synthetic mixtures of pure ammelide, ammeline and melamine at various concentration levels was prepared and then examined by the recommended procedure. The recoveries obtained (given in Table I) were satisfactory and confirm that the absorbances are additive.

INTERFERENCES—

The effect of other constituents of urea pyrolysates such as urea, biuret, triuret, cyanuric acid and guanidine on the determination of the amino-*s*-triazines was examined. The

TABLE I

RECOVERIES OF AMMELIDE, AMMELINE AND MELAMINE FROM SYNTHETIC MIXTURES

Added			Recovered			Absolute error		
Ammelide, per cent.	Ammeline, per cent.	Melamine, per cent.	Ammelide, per cent.	Ammeline, per cent.	Melamine, per cent.	Ammelide, per cent.	Ammeline, per cent.	Melamine, per cent.
59·4	20·8	19·9	59·8	20·7	20·6	+0·4	−0·1	+0·7
58·9	11·2	29·9	58·7	11·0	30·8	−0·2	−0·2	+0·9
29·7	40·0	30·3	29·5	39·0	31·4	−0·2	−1·0	+1·1
39·0	10·2	50·8	38·5	9·4	51·8	−0·5	−0·8	+1·0
50·0	39·5	10·5	49·9	39·3	11·0	−0·1	−0·2	+0·5
			Mean absolute error, per cent. ..			0·3	0·5	0·9

absorbances of solutions of the individual compounds at various concentration levels were measured at a wavelength of 221 nm in phosphate buffer and at 229 and 240 nm in 1·95 N hydrochloric acid. From the results (given in Table II) it was concluded that if the absorbances of these compounds are additive with those of the amino-*s*-triazines, then biuret, triuret and cyanuric acid will interfere, the extent of the interference being significant only when relatively high concentrations of these compounds are present.

TABLE II

ABSORBANCES OF VARIOUS OTHER UREA DECOMPOSITION PRODUCTS UNDER CONDITIONS OF TEST

Compound	Concentration/ mg per 100 ml of final solution	Absorbance in phosphate buffer (1-cm cell) at 221 nm	Absorbance in 1·95 N hydrochloric acid (1-cm cell) at		
			215 nm	229 nm	240 nm
Urea	1	Nil	Nil	Nil	Nil
	5	Nil	Nil	Nil	Nil
	10	Nil	Nil	Nil	Nil
Biuret	2	0·003	—	—	—
	5	0·008	—	—	—
	10	0·016	0·089	0·001	Nil
	25	—	0·224	0·004	Nil
	50	—	0·445	0·008	Nil
Triuret	1	0·029	0·138	0·004	0·001
	2·5	0·069	0·345	0·008	0·002
	5	0·138	0·689	0·013	0·004
Cyanuric acid	2	0·005	—	—	—
	5	0·016	—	—	—
	10	0·033	0·060	0·004	0·001
	25	—	0·138	0·009	0·002
	50	—	0·271	0·015	0·002
Guanidine carbonate	1	Nil	Nil	Nil	Nil
	5	Nil	Nil	Nil	Nil
	10	Nil	Nil	Nil	Nil

Analysis of a series of synthetic mixtures, in which the amino-*s*-triazines formed a major proportion of the sample, demonstrated that interferences caused by biuret, triuret and cyanuric acid can be neglected when these compounds are present at concentrations below about 10 per cent. (Table III).

For the determination of low concentrations of ammeline and melamine in the presence of relatively large amounts of biuret, triuret or cyanuric acid (*e.g.*, in crude biuret or cyanuric acid) the procedure was extended to include corrections for interference by these compounds. In the modified procedure an additional absorbance measurement was made on the strongly acidic solution at 215 nm, where triuret was found to have an appreciable absorbance (see Table II), and the solution of four simultaneous equations [equations (4), (5), (6) and (7) under Calculation] yields accurate values for ammelide, ammeline and melamine and a semi-quantitative value (±25 per cent. relative) for triuret. The equations include terms for cyanuric acid and biuret that permit corrections to be made for the interference by these

TABLE III

RECOVERIES OF AMMELIDE, AMMELINE AND MELAMINE FROM SYNTHETIC MIXTURES CONTAINING OTHER UREA DECOMPOSITION PRODUCTS

Added, per cent.						Recovered, per cent.			Absolute error, per cent.		
Biuret	Triuret	Cyanuric acid	Ammelide	Ammeline	Melamine	Ammelide	Ammeline	Melamine	Ammelide	Ammeline	Melamine
9·4	—	—	44·8	35·7	10·1	43·9	35·4	10·5	−0·9	−0·3	+0·4
—	8·7	—	44·5	36·3	10·5	44·1	36·0	11·0	−0·4	−0·3	+0·5
—	—	9·0	44·9	35·9	10·2	45·3	35·5	10·8	+0·4	−0·4	+0·6
8·3	7·4	7·6	38·8	30·5	7·4	38·9	30·5	7·4	+0·1	0	0

compounds once their concentrations have been determined independently by the methods of Ellis and Formaini[14] and Kazarnovskii and Lebedev,[15] respectively.

On application of this modified procedure to the analysis of two mixtures that simulated urea pyrolysates containing low levels of ammeline and melamine, satisfactory results (which are given in Table IV) were obtained.

TABLE IV

RESULTS OF ANALYSIS OF SYNTHETIC MIXTURES CONTAINING LOW CONCENTRATIONS OF AMMELINE AND MELAMINE

	A		B	
	Present, per cent.	Recovered, per cent.	Present, per cent.	Recovered, per cent.
Ammelide	20·2	19·8	10·0	10·0
Ammeline	5·1	4·9	2·0	2·0
Melamine	5·1	5·2	0·52	0·58
Urea	10·1	—	20·0	—
Biuret	30·4	—	15·0	—
Triuret	8·9	6·8	5·0	4·5
Cyanuric acid	20·2	—	20·0	—
Guanidine cyanurate	—	—	27·5	—

PROCEDURE

APPARATUS—

All calibrated glassware used should be within the B.S. Grade A tolerance.

Ultrasonic bath—A Mettler model ME 1·5 is suitable.

Unicam SP3000 spectrophotometer.

Unicam SP3001 automatic digital printer.

Unicam SP3003 automatic wavelength selector.

Unicam SP3007 constant-temperature cell holder—The temperature of the block of the cell holder was maintained at 25 °C by water circulating from a Churchill laboratory thermocirculator.*

Water-bath—This was controlled thermostatically at 25 °C.

REAGENTS—

All reagents should be of analytical-reagent grade except where stated; distilled, not de-ionised, water must be used throughout. Solid standards and samples must be ground to pass a B.S.S. 100-mesh sieve.

Hydrochloric acid, N.

Hydrochloric acid, 4 N.

Sodium hydroxide, N *solution.*

Sodium hydroxide, 0·1 N *solution*—This solution must be freshly prepared immediately before use by dilution of the N sodium hydroxide solution.

Phosphate buffer solution—Dissolve 136 g of potassium dihydrogen orthophosphate in about 600 ml of water and then transfer the solution to a 1-litre calibrated flask. Add 200·0 ml of N hydrochloric acid and dilute to the calibration mark with water, mixing thoroughly.

*Supplied by Churchill Instrument Company Limited, Perivale, Greenford, Middlesex.

Standard ammelide solution (1 *ml* ≡ 0·1 *mg of ammelide*)—Transfer 100·0 mg of pure ammelide to each of three 500-ml iodine flasks. Add to each flask 100·0 ml of N sodium hydroxide solution. Support the flasks, at an angle of approximately 45°, in an ultrasonic bath containing water at 50 °C, then switch on the current. After 10 minutes remove the flasks from the bath and cool them. Transfer the solutions to 1-litre calibrated flasks, then dilute each to the calibration mark with water and mix well.

Standard ammeline solution (1 *ml* ≡ 0·1 *mg of ammeline*)—Use pure ammeline and prepare exactly as described for standard ammelide solution.

Standard melamine solution (1 *ml* ≡ 0·1 *mg of melamine*)—Use Organic Analytical Standard grade (OAS) melamine and prepare exactly as described for standard ammelide solution.

Standard biuret solution (1 *ml* ≡ 1·0 *mg of biuret*)—Transfer 250 mg of recrystallised biuret to a 250-ml calibrated flask and dissolve it in 25·0 ml of N sodium hydroxide solution. Dilute to the calibration mark with water and mix well.

Standard cyanuric acid solution (1 *ml* ≡ 1·0 *mg of cyanuric acid*)—Dissolve 250 mg of recrystallised cyanuric acid in 25·0 ml of N sodium hydroxide solution and about 175 ml of water. If necessary, warm to ensure complete dissolution, then cool. Transfer the solution to a 250-ml calibrated flask, then dilute to the calibration mark with water and mix.

Standard triuret solution (1 *ml* ≡ 0·5 *mg of triuret*)—Dissolve 50 mg of pure triuret in 100·0 ml of 0·1 N sodium hydroxide solution.

DETERMINATION OF ABSORPTION COEFFICIENTS—

The absorption coefficients used in the calculation refer to the absorbance in a 1-cm cell of a solution at 25 °C of 1 mg of the pure compound in a final volume of 100 ml.

For the routine determination of the absorption coefficients of the amino-*s*-triazines it is recommended that triplicate one-point calibrations be made at an absorbance value in the optimum range of the instrument. For ammelide, ammeline and melamine prepare reagent blanks in triplicate to contain amounts of reagents identical with those used in the standard and make up to the same volume. For biuret, cyanuric acid and triuret a single reagent blank is adequate.

Ammelide in phosphate buffer, $(ax_1)_{221}$—Transfer with a pipette a 10-ml aliquot from each of the three freshly prepared standard ammelide solutions (1 ml ≡ 0·1 mg of ammelide) to 100-ml calibrated flasks. To each flask add, again by means of a pipette, 25 ml of the phosphate buffer solution, then dilute to the calibration mark with water and mix well. Measure the absorbance of each solution against water in 1-cm light path silica cells at a wavelength of 221 nm.

Determine $(ax_1)_{221}$ by deduction of the mean absorbance of the blanks from the mean absorbance of the ammelide solutions.

Ammelide in 1·95 N *hydrochloric acid*, $(ax_2)_{215,\ 229\ \text{and}\ 240}$—Transfer by pipette a 50-ml aliquot from each of the three freshly prepared standard ammelide solutions (1 ml ≡ 0·1 mg of ammelide) to dry 100-ml calibrated flasks. Dilute to the calibration mark with 4 N hydrochloric acid and mix well. Measure the absorbance of each solution against water in 1-cm light path silica cells at wavelengths of 215, 229 and 240 nm.

Determine $(ax_2)_{215}$, $(ax_2)_{229}$ and $(ax_2)_{240}$ by division by 5 of the difference between the mean absorbance of the blanks at each wavelength and the mean absorbance of the ammelide solutions at the corresponding wavelength.

Ammeline in phosphate buffer, $(ay_1)_{221}$—Use the standard ammeline solution (1 ml ≡ 0·1 mg of ammeline) and determine $(ay_1)_{221}$ as given under *Ammelide in phosphate buffer*.

Ammeline in 1·95 N *hydrochloric acid*, $(ay_2)_{215\ \text{and}\ 240}$—Transfer by pipette a 10-ml aliquot from each of the three freshly prepared standard ammeline solutions (1 ml ≡ 0·1 mg of ammeline) to dry 100-ml calibrated flasks. To each flask add, again by means of a pipette, 50 ml of 4 N hydrochloric acid, then dilute to the calibration mark with 0·1 N sodium hydroxide solution and mix well. Measure the absorbance of each solution against water in 1-cm light path silica cells at wavelengths of 215 and 240 nm.

Determine $(ay_2)_{215}$ and $(ay_2)_{240}$ by deduction of the mean absorbance of the blanks from the mean absorbance of the ammeline solutions at the corresponding wavelengths.

Ammeline in 1·95 N *hydrochloric acid*, $(ay_2)_{229}$—Transfer a 10-ml aliquot from each of the three freshly prepared standard ammeline solutions (1 ml ≡ 0·1 mg of ammeline) to dry

200-ml calibrated flasks. To each flask add, by means of a pipette, 100 ml of 4 N hydrochloric acid, then dilute to the calibration mark with 0·1 N sodium hydroxide solution and mix well. Measure the absorbance of each solution against water in 1-cm light path silica cells at a wavelength of 229 nm.

Determine $(ay_2)_{229}$ by multiplying by 2 the difference between the mean absorbance of the blanks and the mean absorbance of the ammeline solutions.

Melamine in phosphate buffer, $(az_1)_{221}$—Use the standard melamine solution (1 ml ≡ 0·1 mg of melamine) and determine $(az_1)_{221}$ by the method given under *Ammelide in phosphate buffer*.

Melamine in 1·95 N *hydrochloric acid*, $(az_2)_{215,\ 229\ \text{and}\ 240}$—Use the standard melamine solution and determine the absorption coefficients as outlined under *Ammeline in* 1·95 N *hydrochloric acid*, on this occasion measuring also at 229 nm.

Biuret in phosphate buffer, $(ab_1)_{221}$—Use a 10-ml aliquot of freshly prepared standard biuret solution (1 ml ≡ 1·0 mg of biuret) and proceed as outlined under *Ammelide in phosphate buffer*, but divide by 10 the difference between the blank and the biuret solution absorbances.

Biuret in 1·95 N *hydrochloric acid*, $(ab_2)_{215,\ 229\ \text{and}\ 240}$—Use a 50-ml aliquot of freshly prepared standard biuret solution (1 ml ≡ 1·0 mg of biuret) and proceed as outlined under *Ammelide in* 1·95 N *hydrochloric acid*, but divide by 50 the difference between the absorbance of the blank at each wavelength and the absorbance of the biuret solution at the corresponding wavelength.

Cyanuric acid in phosphate buffer, $(ah_1)_{221}$—Use a 10-ml aliquot of the standard cyanuric acid solution (1 ml ≡ 1·0 mg of cyanuric acid) and proceed as outlined under *Ammelide in phosphate buffer*, but divide by 10 the difference between the blank and cyanuric acid solution absorbances.

Cyanuric acid in 1·95 N *hydrochloric acid*, $(ah_2)_{215,\ 229\ \text{and}\ 240}$—Use a 50-ml aliquot of the standard cyanuric acid solution (1 ml ≡ 1·0 mg of cyanuric acid) and proceed as outlined under *Ammelide in* 1·95 N *hydrochloric acid*, but divide by 50 the difference between the absorbance of the blank at each wavelength and the absorbance of the cyanuric acid solution at the corresponding wavelength.

Triuret in phosphate buffer, $(at_1)_{221}$—Use a 10-ml aliquot of freshly prepared standard triuret solution (1 ml ≡ 0·5 mg of triuret) and proceed as outlined under *Ammelide in phosphate buffer*, but divide by 5 the difference between the blank and triuret solution absorbances.

Triuret in 1·95 N *hydrochloric acid*, $(at_2)_{215,\ 229\ \text{and}\ 240}$—Use a 10-ml aliquot of freshly prepared standard triuret solution (1 ml ≡ 0·5 mg of triuret) and proceed as outlined under *Melamine in* 1·95 N *hydrochloric acid*, but divide by 5 the difference between the absorbance of the blank at each wavelength and the absorbance of the triuret solution at the corresponding wavelength.

Preparation of sample solution—

Transfer a suitable weight (see Note 1) of sample to each of three 500-ml iodine flasks and add to each 100·0 ml of N sodium hydroxide solution. Support the flasks at an angle of approximately 45° in an ultrasonic bath containing water at 50 °C, then switch on the current.

After 10 minutes remove the flasks from the bath and cool them. Transfer the solutions to 1-litre calibrated flasks, then dilute each to the calibration mark with water and mix the contents well.

Absorbance measurements in phosphate buffer—

Transfer with a pipette a 10-ml aliquot from each of the prepared sample solutions to 100-ml calibrated flasks. To each flask add, again by means of a pipette, 25 ml of the phosphate buffer solution, then dilute to the calibration mark with water and mix well. Prepare concurrently a reagent blank in triplicate by using of a 10-ml aliquot of 0·1 N sodium hydroxide solution instead of the sample solution. Measure the absorbance of each solution against water in 1-cm light path silica cells at a wavelength of 221 nm.

Determine the absorbance at 221 nm by deducting the mean absorbance reading of the blanks from the mean absorbance reading of the sample solutions.

ABSORBANCE MEASUREMENTS IN 1·95 N HYDROCHLORIC ACID—

Transfer a suitable amount (see Note 2) from each of the prepared sample solutions to dry 100-ml calibrated flasks. To each flask add, by means of a pipette, 50 ml of 4 N hydrochloric acid, then dilute to the calibration mark with 0·1 N sodium hydroxide solution and mix well. Prepare concurrently a reagent blank in triplicate by transferring 50-ml portions of 4 N hydrochloric acid to dry 100-ml calibrated flasks, then diluting to the calibration mark with 0·1 N sodium hydroxide solution and mixing well. Measure the absorbance of each solution, against water, in 1-cm light path silica cells at wavelengths of 229, 240 and, if a semi-quantitative value for triuret is required, 215 nm.

Determine the absorbances at 229 and 240 nm and, if required, at 215 nm by deducting the mean absorbance readings of the blanks at each wavelength from the mean absorbance reading of the sample solution at the corresponding wavelength.

CALCULATION—

For samples containing large amounts of amino-*s*-triazines and less than 10 per cent. w/w each of biuret, triuret and cyanuric acid, the calculation involves the solution of three simultaneous equations—

$$\frac{100 \times (A_1)_{221}}{q} = [(ax_1)_{221} \times Cx] + [(ay_1)_{221} \times Cy] + [(az_1)_{221} \times Cz] \quad (1)$$

$$\frac{100 \times (A_2)_{229}}{p} = [(ax_2)_{229} \times Cx] + [(ay_2)_{229} \times Cy] + [(az_2)_{229} \times Cz] \quad (2)$$

$$\frac{100 \times (A_2)_{240}}{p} = [(ax_2)_{240} \times Cx] + [(ay_2)_{240} \times Cy] + [(az_2)_{240} \times Cz] \quad (3)$$

where q mg is the amount of sample in 100 ml of phosphate-buffered solution, p mg is the amount of sample in solution in 100 ml of 1·95 N hydrochloric acid, $(A_1)_{221}$ is the absorbance of the sample solution at 221 nm, $(A_2)_{229}$ is the absorbance of the sample solution at 229 nm, $(A_2)_{240}$ is the absorbance of sample solution at 240 nm, Cx is the percentage of ammelide in the sample, Cy is the percentage of ammeline in the sample, Cz is the percentage of melamine in the sample and $(ax_1)_{221}$ to $(az_2)_{240}$ are the absorption coefficients.

For samples containing less than 5 per cent. w/w of ammeline and melamine and relatively large amounts of triuret, cyanuric acid and biuret, the calculation is extended to include an estimation of triuret and corrections for biuret and cyanuric acid—

$$\frac{100 \times (A_1)_{221}}{q} = [(ax_1)_{221} \times Cx] + [(ay_1)_{221} \times Cy] + [(az_1)_{221} \times Cz] + [(ab_1)_{221} \times Cb] + [(ah_1)_{221} \times Ch] + [(at_1)_{221} \times Ct] \quad (4)$$

$$\frac{100 \times (A_2)_{215}}{p} = [(ax_2)_{215} \times Cx] + [(ay_2)_{215} \times Cy] + [(az_2)_{215} \times Cz] + [(ab_2)_{215} \times Cb] + [(ah_2)_{215} \times Ch] + [(at_2)_{215} \times Ct] \quad (5)$$

$$\frac{100 \times (A_2)_{229}}{p} = [(ax_2)_{229} \times Cx] + [(ay_2)_{229} \times Cy] + [(az_2)_{229} \times Cz] + [(ab_2)_{229} \times Cb] + [(ah_2)_{229} \times Ch] + [(at_2)_{229} \times Ct] \quad (6)$$

$$\frac{100 \times (A_2)_{240}}{p} = [(ax_2)_{240} \times Cx] + [(ay_2)_{240} \times Cy] + [(az_2)_{240} \times Cz] + [(ab_2)_{240} \times Cb] + [(ah_2)_{240} \times Ch] + [(at_2)_{240} \times Ct] \quad (7)$$

where $(A_2)_{215}$ is the absorbance of the sample solution at 215 nm, Cb is the percentage of biuret in the sample, Ch is the percentage of cyanuric acid in the sample, Ct is the percentage of triuret in the sample and the values $(ax_1)_{221}$ to $(at_2)_{240}$ are the absorption coefficients determined.

The concentrations of biuret (*Cb*) and cyanuric acid (*Ch*) are determined independently by methods based on those of Ellis and Formaini[14] and Kazarnovskii and Lebedev,[15] respectively.

NOTES—

1. The sample weight is normally chosen so that the highest absorbance measured in the phosphate-buffered solution lies in the range from 0·5 to 1·0 absorbance unit. Thus, for samples in which the amino-*s*-triazines form a major proportion of the sample a suitable weight is 0·100 g, while for samples containing minor amounts of ammeline and melamine up to 1 g can be taken.

2. An amount of solution between 5 and 50 ml is chosen such that the highest absorbance at any of the analytical wavelengths is in the range from 0·5 to 1·0 absorbance unit. The optimum volume can best be determined after a preliminary test in which the absorbance in 1·95 N hydrochloric acid from a 10-ml portion of sample solution is measured.

CONCLUSIONS

In the ultraviolet spectrophotometric method developed for the simultaneous determination of ammelide, ammeline and melamine, interferences from other urea decomposition products are minimised by making absorbance measurements at low pH values. It is necessary to correct for the effect of triuret, biuret and cyanuric acid only when these compounds are present in significant amounts. The procedure can be adapted to the analysis of samples of widely varying composition and has been used for the analysis of urea pyrolysates containing both large and small amounts of the three amino-*s*-triazines. It is considered that the accuracy of the method is at least as good as, and in most cases better than, any previously reported in the literature for the determination of ammelide and ammeline. Although more precise results have been reported for the determination of melamine by using gravimetric procedures based on precipitation of the water-insoluble melamine cyanurate, these procedures can be applied directly only to the determination of water-soluble melamine. When melamine is present in a sample as melamine cyanurate rather lengthy separation techniques are required to remove cyanurate before the gravimetric finish can be applied. As melamine cyanurate is soluble in both acidic and alkaline solution the recommended procedure has the advantage that total melamine, inclusive of any present as the cyanurate, is measured.

Although the calibration procedure required for the determination of the absorption coefficients is quite lengthy the stability of the SP3000 is such that these coefficients need be determined only once every 6 months. If a computer is used to solve the sets of three or four simultaneous equations a sample can be analysed in less than 1 hour, and the analysis of 12 samples completed in 1 day, by a single operator.

The authors express their thanks to Dr. A. C. Docherty for interest and encouragement in the work. Particular thanks are also due to Miss P. A. Watson and Messrs. W. Johnson and S. N. Das for experimental assistance in the development of the method, to Mr. G. Trenholm who prepared the samples of triazines and to Mr. M. Adamson for providing the computer programme.

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NOTE—Reference 1 is to Part I of this series.

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A Computer Method for the Spectrophotometric Determination of Overlapping pK_a Values

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A least-squares computer method has been developed to obtain two pK_a values from spectrophotometric data in instances when the values are so close together that the calculations usually applied for individual pK_a values are not appropriate. A scaling procedure improves the condition of the matrix that is constructed in solving the sets of simultaneous equations. Two examples of applications of the method are given.

The advantages of spectrophotometric methods for determining acidic and basic dissociation constants, and details of the experimental techniques, have been discussed elsewhere.[1] However, difficulties arise when a substance has two ionising groups that have pK_a values lying within three logarithmic units of each other. In such an instance, for the system—

$$A + H^+ \rightleftharpoons B; \qquad K_{a1} = [H^+][A]/[B]$$
$$B + H^+ \rightleftharpoons C; \qquad K_{a2} = [H^+][B]/[C]$$

ϵ_A and ϵ_C can usually be obtained by making measurements at high and low pH, respectively, but ϵ_B is not directly available. For example, if pK_{a1} and pK_{a2} differ by 1·2, the maximum fraction of the species that can be present as B can never exceed two-thirds.

It is possible to calculate ϵ_B, K_{a1} and K_{a2} by successive approximations[1] but this method is tedious. Alternative procedures are available[2,3] for those instances when the graph of absorbance *versus* pH passes through a maximum or a minimum in the region where the species B predominates. More generally, if measurements are made of the absorbances of the solutions at suitably spaced pH values, then values of ϵ_B, K_{a1} and K_{a2} can be found by solving three simultaneous equations. This method has the disadvantage that undue significance is attached to these three points while the other experimental results are ignored. Roth and Bunnett[4] extended this approach to include ϵ_A and ϵ_C as unknowns by taking five points on the graph of optical density *versus* pH and solving five simultaneous equations by using a computer. In this paper we describe a method in which all the experimental data are used to solve for ϵ_B, K_{a1} and K_{a2} by a least-squares minimisation of their fit to the computed graph of absorbance *versus* pH.

Method

At each of n experimental points, the relationship

$$-hD_B + (D - D_A)\,K_{a1} + h^2\,(D - D_C)/K_{a2} + hD = 0$$

is valid, where D_A, D_B and D_C are the absorbances of pure A, B and C, respectively, and D is the measured absorbance, at the selected wavelength, h is 10^{-pH}, and K_{a1} and K_{a2} are as defined above. The three unknowns are obtained by solving the set of n simultaneous equations by a matrix transposition technique with a computer library subroutine[5] based on the method of Golub.[6] Initially, differences in the orders of magnitudes between the columns of the matrix led to poor conditioning. This difficulty was overcome by using a scaling technique so that the maximum modulus of any element in the matrix was unity. The computer programme has been written in Fortran 4E, for use on an IBM 360/50 digital computer. The printed output includes the values of D_B, pK_{a1}, pK_{a2}, the standard error of the fit, and a tabulation of observed and calculated absorbances, with their differences.

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EXPERIMENTAL AND RESULTS

The method described has been in routine use in this Department for more than a year. Figs. 1 and 2 give examples of the application of the method in the instances when ϵ_B has a value intermediate between those of ϵ_A and ϵ_C and when ϵ_B is greater than either ϵ_A or ϵ_C.

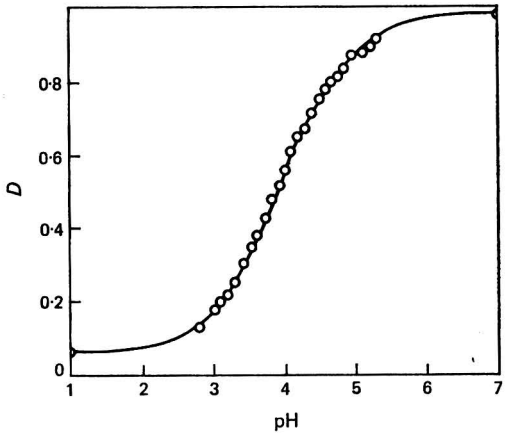

Fig. 1. Graph of D_{1cm}^{280nm} *versus* pH for a 4×10^{-5} M benzidine solution. The solid line is the computed curve

The results given in Fig. 1 were obtained for 4×10^{-5} M benzidine (AnalaR) solution at 20 °C in buffers with an ionic strength of 0·01.[7] Readings were taken at 280 nm in 1·00-cm cells on a Unicam SP500 spectrophotometer, and the pH values were checked on a Cambridge pH meter. The absorbance of the di-cation (0·067) was obtained from readings at pH 0 and 1, and for the neutral molecule (0·972) the mean of values obtained at pH 7 and 8 was used. Computer analysis of the data gave $pK_{a1} = 4{\cdot}676$, $pK_{a2} = 3{\cdot}712$, $D_B = 0{\cdot}695$, and a value of 0·011 for the standard error of fit. Under comparable conditions, but operating at 300 nm, Albert and Serjeant[1] obtained values of $pK_{a1} = 4{\cdot}70$ and $pK_{a2} = 3{\cdot}63$ by using a method of successive approximations. Application of the computer method to their data gave values of $pK_{a1} = 4{\cdot}63$ and $pK_{a2} = 3{\cdot}51$.

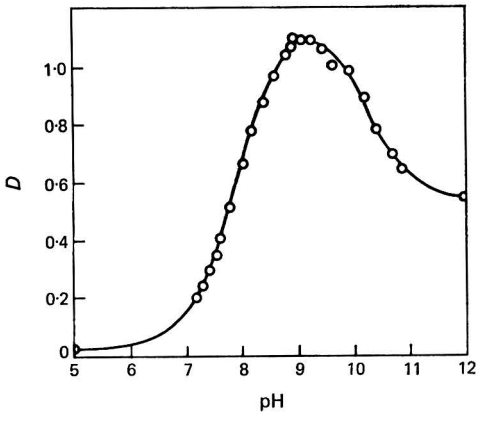

Fig. 2. Graph of D_{1cm}^{586nm} *versus* pH for a 3×10^{-5} M catechol violet solution. The solid line is the computed curve

When measurements were made on catechol violet, the results for which are shown in Fig. 2, hydroxylamine (0·01 M) was included in the stock solution to minimise oxidation by air. The catechol violet was B.D.H. laboratory-reagent grade. The analytical wavelength was 586 nm, and the absorbance of the pure species was determined to be 0·022 at pH 4·3 and 5·0, and 0·537 at pH 12·0, for a 3×10^{-5} M solution. Analysis of the results gave $pK_{a_1} = 10{\cdot}230$ and $pK_{a_2} = 7{\cdot}921$ at 20 °C and $I = 0{\cdot}01$, with a standard error of fit of 0·019. Because the borate ion forms chelates with catechol violet, glycine buffers were used instead of borax buffers over the pH range 9·0 to 9·7. Ryba, Cifka, Malat and Suk[8] obtained pK_{a_1} and pK_{a_2} values of 9·76 and 7·82, respectively, by potentiometric measurements at $I = 0{\cdot}2$ and room temperature, and 9·80 and 7·81 by colorimetric measurements under the same conditions. For the latter results they solved simultaneous equations for selected pairs of points on the graph of absorbance *versus* pH.

A listing of the computer programme is available from the authors on request.

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The Determination of Nitric Oxide and Nitrogen Dioxide in Flue Gases

Part I. Sampling and Colorimetric Determination

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Methods for the determination of nitric oxide and nitrogen dioxide have been evaluated for the analysis of flue gases from natural gas combustion systems: these methods have been modified where necessary. The study has included both manual and continuous instrumental methods of analysis; manual sampling and colorimetric methods are described here and continuous instrumental methods in Part II (p. 64).

The increasing interest in environmental pollution has emphasised the importance of particular combustion products. It is well known that nitric oxide and nitrogen dioxide are emitted in the flue gases of combustion systems and may frequently be present in concentrations of several hundred parts per million. Rapid and accurate methods are, therefore, essential for the control monitoring of these oxides and for research purposes.

Several techniques have been reported for the determination of nitric oxide and nitrogen dioxide, including infrared and ultraviolet spectroscopy,[1–3] mass spectrometry[4] and various chemical[5,6] and electrochemical methods.[7] All instrumental methods require calibration against an independent chemical method. A classical method for determining total nitrogen oxides (excluding nitrous oxide) is based on the reaction of phenoldisulphonic acid with the nitrate formed by peroxide oxidation of the nitrogen oxides to give a yellow solution.[5] This method is time-consuming and does not differentiate between nitric oxide and nitrogen dioxide. To meet this requirement and to provide a rapid procedure for on-line and individual determinations a method based on the use of an absorption reagent described by Saltzman[6,8] has been studied.

The reactive nature of nitrogen oxides leads to problems in the sampling of flue gases. There are many reports in the literature describing investigations of the catalytic reduction of nitric oxide present by combustion products of a chemically reducing nature.[9–19] Several reactions can be postulated, a typical one being

$$NO + CO \xrightarrow{\text{catalyst}} CO_2 + \tfrac{1}{2}N_2$$

When other reducing agents, *e.g.*, methane, are present, other equations are necessary to describe the processes that occur. Under uncatalysed conditions this reaction proceeds at a negligible rate, at least at temperatures up to about 800° C. However, in the presence of a suitable catalyst and at temperatures below 800 °C, it can proceed to about 90 per cent. completion in about 0·1 s with the concentrations of nitrogen oxides and carbon monoxide that can be encountered in gaseous combustion products (see, for example, Shelef, Otto and Gandhi[19]). A considerable number of catalysts have been found to be effective in promoting the reaction; many transition metals and transition metal oxides, either singly or in admixture, have been shown to be particularly effective.[9–19]

In view of the above observations a study of possible interference in the analytical measurement of nitrogen oxides by catalytic reduction on metal sampling probes seemed to be necessary.

Experimental

One of the most widely used chemical methods for the determination of nitrogen dioxide is the colorimetric method of Saltzman, which was first published in 1954[6] and modified in 1960[8] to increase the rate of colour development. The basic method enables nitrogen dioxide to be determined by its reaction with sulphanilic acid in acetic acid, the reaction

product being coupled with *N*-1-naphthylethylenediamine *in situ* to give a red dye. The colour is evaluated spectrophotometrically and the value obtained is converted into a numerical amount by reference to a previously prepared calibration graph.

During the reaction some of the nitrogen dioxide reacts with water to form nitric and nitrous acids, the former taking no part in the diazotisation reaction. According to Saltzman the over-all "loss" in the reactions leading to dye formation amounts to 28 per cent. of the total; a factor of 0·72 must therefore be applied to the calibration results if sodium nitrite is used for calibration. The magnitude of this factor has been questioned by Kooiker, Schuman and Chan,[20] and by Stratmann and Buck.[21] However, recent work by Shaw[22] supports the original factor of 0·72. In order to verify this factor, known volumes of nitric oxide produced by the electrolysis of nitrosyl hydrogen sulphate[23] were chemically oxidised as described in the general procedure, and the resulting nitrogen dioxide was measured by the Saltzman procedure. The results are shown in Table I.

TABLE I

SALTZMAN FACTOR: CHEMICAL OXIDATION OF NITRIC OXIDE

Concentration of nitric oxide		Oxidant efficiency	Factor assuming	
Liquid phase/ $\mu g\ ml^{-1}$ of absorbent	Gas phase, p.p.m. v/v	assuming factor of 0·72, per cent.	100 per cent. oxidant efficiency	
2·81	94	100	0·72	
0·93	93	104	0·75	0·74
0·49	98	103	0·74	
0·25	98	104	0·75	
0·77	46	103	0·74	
0·71	95	100	0·72	0·73
0·80	320	100	0·72	
0·64	482	103	0·74	

The value for the Saltzman factor is not fully proved by this method because of the interdependence of the factor and the oxidant efficiency. However, it is significant that this efficiency does not rise greatly above 100 per cent. when using a factor of 0·72, even with 10-fold changes in gas phase and final liquid-phase concentrations. Further experiments in which measured volumes of nitric oxide were oxidised overnight by air in the presence of the reagent also showed the factor to be 0·72. Although this work verifies Saltzman's factor, it is possible that different values obtained by other workers[20,21] are attributable to minor variations in reaction conditions.

OXIDATION OF NITRIC OXIDE TO NITROGEN DIOXIDE—

The determination of both nitric oxide and nitrogen dioxide necessitates the determination of the nitrogen dioxide before and after an oxidation step in which nitric oxide is oxidised to nitrogen dioxide. This oxidation was therefore examined in detail, in order to obtain accurate results for both gases by the Saltzman procedure.

Several analytical methods have been reported in the literature, in which various pressures of air or oxygen were used to convert the nitric oxide into nitrogen dioxide.[24] To study this method of oxidation nitric oxide was injected into a 200-ml glass torpedo containing 20 ml of Saltzman reagent and a selected nitrogen - oxygen mixture. The reaction was allowed to proceed for a given time before running off the reagent and measuring its optical density. The curves in Fig. 1 show the increased rate of oxidation when using pure oxygen instead of 1 + 1 nitrogen - oxygen mixtures and also the effect of pressure on the rate of oxidation. The process, however, is too lengthy to be used as a control method.

Nitric oxide is oxidised by several common oxidants such as dichromates or permanganates, which are used as bulk solutions or as moist solids on an inert support. Many conflicting reports have been published based on these systems[25–27] but none of the oxidants used appears to be fully efficient and reliable over long periods. The most successful of the published methods was that of Bethell, Shaw and Thomas,[27] but when this method was applied in the present work the initially high efficiency of this oxidant soon diminished. Various chemical oxidation systems were examined, including potassium dichromate - sulphuric acid on glass beads and on lightly ground chromium trioxide plates. Most systems gave low oxidation efficiency at nitric oxide concentrations above 100 p.p.m.

The most successful oxidation system tested consisted of sodium dichromate - sulphuric acid on glass beads. The oxidant is prepared by dissolving sodium dichromate in concentrated sulphuric acid and a small amount of water. The solution is mixed with glass beads and the mixture is heated at 110 °C to remove excess of water. The oxidant is then maintained at 65 °C and at constant humidity by flushing with a carrier gas that has a constant water content. The maintenance of the oxidant at the correct moisture level is critical.

It was found that with prolonged use the efficiency of the oxidant could be impaired by very wet flue gases, which may contain up to 18 per cent. v/v of water vapour. Analysis of calibration blends passed through the oxidant while dry and then after wetting confirmed this finding. The effect was overcome by diluting the wet flue gas with air before passing it through the oxidant. The sample was diluted by using a sample loop that was flushed by a portion of the oxidant carrier gas. In addition to reducing the effective water content of the sample passing through the oxidant, high nitric oxide concentrations are also diluted. The volume of the sample loop can be chosen to give optimum values in the final colour development.

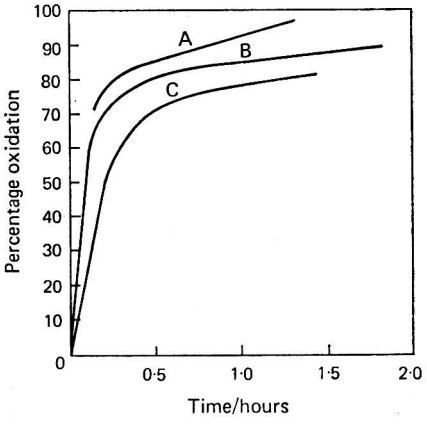


Fig. 1. Oxidation of nitric oxide in presence of Saltzman reagent. Nitric oxide concentration 50 p.p.m. Curve A, oxidation of 10 μl of nitric oxide in 1 + 1 nitrogen - oxygen (2 atmospheres); curve B, oxidation of 10 μl of nitric oxide in 200 ml of oxygen (1 atmosphere); and curve C, oxidation of 10 μl of nitric oxide in 200 ml of 1 + 1 nitrogen - oxygen (1 atmosphere)

GENERAL PROCEDURE—

The apparatus used for the determination of nitric oxide and nitrogen dioxide is shown diagrammatically in Fig. 2. The system is designed for use in three distinct modes. Firstly, for the determination of total nitrogen oxides in combustion systems when no secondary air is used, *i.e.*, for high nitric oxide and water contents, the sample loop system is used. Sample gas is drawn through the sample loop and valve by a simple diaphragm pump. A second pump draws air through a sulphuric acid - water mixture to maintain the heated oxidant at the correct humidity. Operation of the sample valve allows the sample to be flushed from the loop by a portion of the moist air.

Secondly, for low concentrations of total nitrogen oxides, *e.g.*, atmospheric pollution levels, for which an excessively large sample loop would be required, the sample volume is determined by timing the passage of a measured sample flow. As the water contents of these samples are also lower, no dilution is necessary. A 4-way tap connected in the sample and flushing gas lines permits interchange of these through the oxidant for an accurately known time. The sample flow-rate is measured with a soap-film flow meter.

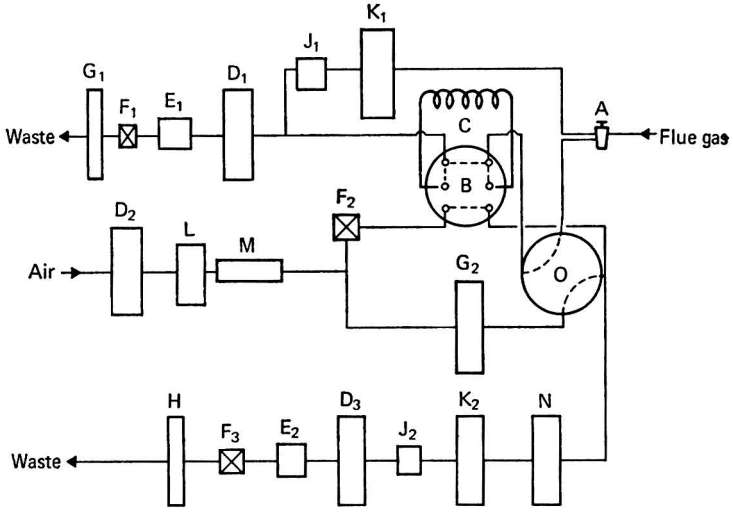
In the third mode, only nitrogen dioxide is determined. A 2-way tap by-passes both the sample loop and oxidant, so that the sample is drawn directly into an absorption vessel where only nitrogen dioxide reacts. The sampling time and the flow-rate of the sample gas are again measured.

When sampling repeatedly from flue gases of high water content, it is advantageous to insert a cold trap to remove water from the sample line so as to prevent build-up of moisture in the system.

SAMPLING—

It is common practice in the investigation of medium and large-scale combustion systems to use stainless-steel probes for sampling combustion products prior to analysis. The design of such sampling probes is variable and depends on the particular type of analysis required. A series of experiments was carried out with a Tunnel Mixing Burner with probe linings consisting of 210-cm × 6-mm i.d. stainless-steel tubing or 210-cm × 4-mm i.d. silica tubing, which gave probe residence times of 4 to 6 s. The gas temperature at the probe inlet, as measured by suction pyrometry, was varied between 800 and 1700 °C and this fell to slightly above ambient temperature at the outlet. In both instances a considerable length of the probe was at a catalytically active temperature, *i.e.*, in the range from about 100 to 800 °C. The design of the probe is shown in Fig. 3. It consists of an electrically heated, water-cooled, stainless-steel probe fitted with either of the above linings.

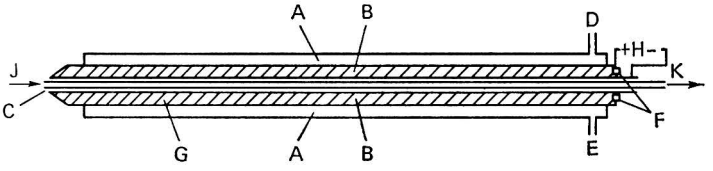
Another important aspect to be considered is the possible oxidation of nitric oxide to nitrogen dioxide by the oxygen present in the flue gas during sampling. To study this effect nitric oxide was electrolytically generated into a stream of nitrogen and, after dilution with known amounts of air, the mixture was analysed by the Saltzman method. The time of reaction was varied by passing the gases through tubes of known volumes at a fixed flow-rate. These experiments showed that a greater degree of oxidation occurred than that calculated from the known rate constant.[28] This effect has not been explained, catalysis



A	= 2-Way tap (NO_x - NO_2)	J_1J_2	= Traps
B	= Sample valve	K_1K_2	= Absorption vessels
C	= Sample loop	L	= Humidifier (H_2SO_4 - H_2O) (1 + 2·5 v/v)
$D_1D_2D_3$	= Tubes containing silica gel	M	= Glass-wool filter
E_1E_2	= Pumps	N	= Oxidiser
$F_1F_2F_3$	= Needle valves	O	= 4-Way tap
G_1G_2	= Flow meters		
H	= Soap-film flow meter		

Fig. 2. Schematic diagram of apparatus for determination of nitric oxide and nitrogen dioxide

being unlikely on non-porous surfaces.[29] However, this work does show that if significant values for nitrogen dioxide contents are required short residence times are essential. For example, a flue gas containing 10 per cent. of oxygen and 700 p.p.m. of nitric oxide was found to contain 100 p.p.m. of nitrogen dioxide after 1 minute.



A = Water-cooled jacket
B = Air space
C = Removable silica tube
D = Cooling water inlet
E = Cooling water outlet
F = Electrical insulators
G = Position of thermocouple hot junction(thermocouple not shown)
H = 12-V d.c. power supply
J = Gas inlet
K = Gas outlet

Fig. 3. Water-cooled, electrically heated sampling probe

METHOD

APPARATUS—

Absorption vessel—This vessel is shown in Fig. 4. The funnel is calibrated at 10·0 and 20·0 ml for the direct addition of reagent. The No. 1 porosity sinter must be chosen with care to provide a uniform flow of gas. A typical absorption vessel has an efficiency better than 97 per cent., which is considered to be satisfactory for most routine applications.

Oxidant tube—This consists of a 20 × 1·2-cm glass tube fitted with a B14 socket inlet and 0·6-cm outlet, plugged with glass-wool, which is heated over its complete length by a heating tape controlled by a thermal switch set at 65 °C.

Humidifier—A Drechsel bottle with a No. 0 porosity sintered-glass inlet and containing 20 ml of concentrated sulphuric acid and 50 ml of water is used. A glass-wool plug filter prevents the escape of spray.

Silica-gel trap—A 15 × 2·5-cm glass tube fitted with a B24 ground-glass joint at one end and 0·6-cm outlet tube at the other, which is filled with 6 to 20-mesh dried silica gel.

Sample valve—A Perkin-Elmer manually operated six-port valve with Teflon rotor.

Sample loops—These are of various sizes and constructed of glass. (For a sample containing about 200 p.p.m. of NO_x a loop of 50-ml volume is required.)

REAGENTS—

Absorption solution—Dissolve 5 g of sulphanilic acid in about 500 ml of nitrite-free water and add 50 ml of glacial acetic acid. Dissolve 0·05 g of *N*-1-naphthylethylenediamine dihydrochloride in a little water, filter the solution into the above solution and dilute to 1 litre.

Sulphuric acid - water—Mix carefully 20 ml of concentrated acid (sp. gr. 1·84) with 50 ml of water.

Oxidant—Dissolve 5 g of sodium dichromate in a mixture of 1 ml of concentrated sulphuric acid and 2 ml of water, add 150 g of 1 mm diameter glass beads and stir until the mixture is uniform. Dry at 110 °C for about 1 hour, with occasional stirring, and finally break up agglomerates before use.

CALIBRATION—

Prepare a standard sodium nitrite solution by dissolving 0·203 g of dried sodium nitrite in water and dilute to 1 litre. With a pipette, introduce 10 ml of this solution into a 100-ml calibrated flask and make the volume up to the mark with water.

1 ml of solution ≡ 10 μl of nitrogen dioxide at 25 °C and 760 mm pressure of mercury. (This takes into consideration a factor of 0·72.)

Place, by pipette, 0·25, 0·5, 0·75 and 1·0 ml of this solution into 20-ml calibrated flasks and make the volumes up to the mark with absorption solution. Allow the solutions to stand for 10 minutes and measure their optical densities in a 1-cm silica or glass cell at 545 nm. Plot a graph of optical density against volume of nitrogen dioxide in microlitres.

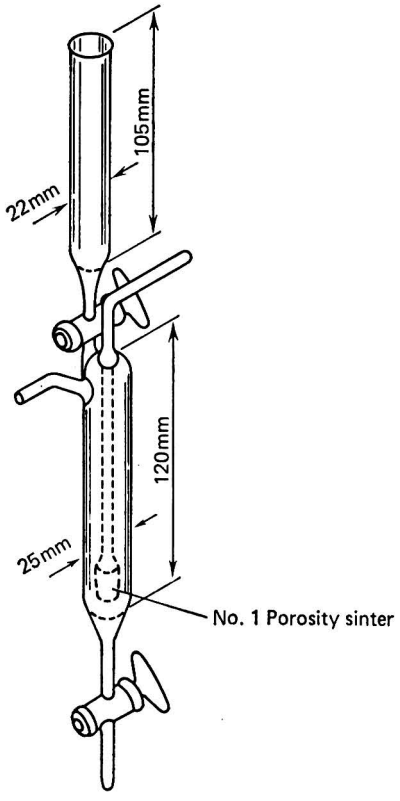


Fig. 4. Absorption vessel

PROCEDURE—

Set up the apparatus as shown diagrammatically in Fig. 2.

(*a*) *Total nitrogen oxides at concentrations greater than* 25 *p.p.m.*—Switch on the oxidant heater and gas pumps. Turn tap O such that moist flushing air passes through the oxidant, adjusting the flow with valve F_3 to 150 ml min^{-1} on the soap-film flow meter, H. Open valve F_2 until the flow meter, G_2, indicates approximately 125 ml min^{-1}. The loop-flushing flow-rate is therefore 25 ml min^{-1}. Turn tap A and sample valve B so that the sample gas is drawn through the sample loop. Adjust this flow, which is indicated on flow meter G_1, to 150 ml min^{-1} by using valve F_1. Allow the system to reach equilibrium and maintain it for about 30 minutes.

Measure 20 ml of reagent into the absorption vessel funnel, K_2, and run the solution into the absorber. Turn the sample valve, B, to flush the sample gas through the oxidant and absorption solution. After flushing for 10 minutes run off the solution and measure the optical density on a suitable instrument at 545 nm by using a 1-cm cell, with the absorption solution as reference.

(*b*) *Total nitrogen oxides at concentrations less than* 25 *p.p.m.*—Set up the sample and flushing gas flows as before, close valve F_2 and place 20 ml of absorption solution in absorption vessel K_2. Turn tap O so that the sample gas passes through the oxidant and the absorption vessel. Measure the flow-rate, which should not exceed 150 ml min^{-1} on the soap-film flow meter, H. After passing sample gas for an accurately timed period, return tap O to its original position and continue flushing the system for 10 minutes. Run off the absorption solution and measure the optical density as before. The product of the sampling time and the flow-rate should be adjusted to give a sample volume containing 5 to 10 μl of nitrogen oxides for maximum accuracy.

(*c*) *Nitrogen dioxide*—Set up the flow-rates as before and place 20 ml of absorption solution in the absorption vessel, K_1. Turn tap A so that sample gas passes directly into the absorption vessel, K_1, for a measured time before returning the tap to its original position. Allow the colour to develop for 10 minutes, run off the solution and measure the optical density as before.

NOTE—Condition the apparatus before use by passing the equivalent of two samples. This operation can be carried out during the latter part of the warm-up period.

CALCULATION—

Convert the optical density readings obtained by each method into microlitres of nitrogen dioxide by reference to the calibration graph. Calculate the concentrations of nitrogen oxides as follows.

Total nitrogen oxides—Substitute the results obtained by procedure (*a*) in the equation—

$$C = \frac{v \times 10^3}{V} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

or by procedure (*b*) in the equation—

$$C = \frac{v \times 10^3}{T \times F} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

where C is the concentration of nitrogen oxides in parts per million v/v at 25 °C and 760 mm pressure of mercury; v is the volume of nitrogen dioxide in microlitres from the graph; V is the volume of sample loop in millilitres at 25 °C and 760 mm pressure of mercury; T is the sampling time in minutes; and F is the indicated flow-rate in millilitres per minute at 25 °C and 760 mm pressure of mercury.

Nitrogen dioxide—Substitute the results obtained by procedure (*c*) in equation (2).

Nitric oxide—Subtract the concentration of nitrogen dioxide from the concentration of total nitrogen oxides—

$$C_{NO} = C_{total} - C_{NO_2} \quad .. \quad .. \quad .. \quad .. \quad (3)$$

These concentrations are expressed as parts per million v/v in sample gas saturated with water vapour at 25 °C and 760 mm pressure of mercury.

RESULTS AND DISCUSSION

ACCURACY AND REPEATABILITY—

The procedure described has been used to determine nitric oxide and nitrogen dioxide in a large number of prepared blends and in the flue gases of various burner systems. The analytical results obtained for several blends are compared below with the calculated values.

Concentration of nitric oxide, p.p.m.—

Calculated	45	88	138	211	272	292	361	570	863	1500
Found	45	85	137	210	270	300	352	568	860	1470

The blends were prepared by mixing measured flow-rates of pure nitric oxide with nitrogen. These results show that the method is applicable over a wide range of nitric oxide concentrations, and that the oxidant retains a high efficiency.

A series of results for total nitrogen oxides produced by a Tunnel Mixing Burner operating under steady conditions on a natural gas - air mixture is shown below.

Total nitrogen oxides, p.p.m.	234	228	225	236	224	218	224	225	216	224	228	224

Mean 226 Standard deviation 1·63

A single determination by the prescribed method can be completed in about 15 minutes.

INFLUENCE OF PROBE MATERIAL—

In the studies involving the use of different probe materials a Tunnel Mixing Burner fired on a natural gas - air mixture was used. The results are given in Table II.

Analysis of samples of oxidising combustion products withdrawn through silica and stainless-steel probes gave results which, within the accuracy of the analytical technique, were independent of the probe material. This is shown in Table II (run Nos. 1 and 2). The proportion of the stoicheiometric amount of air used to obtain the combustion products from runs 1 and 2 was 110 per cent.

Analysis of samples of reducing combustion products, on the other hand, gave results that differed greatly according to the probe material used. This is shown in Table II (run Nos. 3 to 13), from which it is seen that under reducing conditions sampling through stainless-steel probes can lead to large losses of the nitrogen oxides originally present. The losses observed in the present work were usually in excess of 90 per cent. These results indicate that catalytic reduction within metal probes can interfere in the determination of nitrogen oxides, and this interference is of such magnitude that in some circumstances it can completely invalidate the analytical measurements.

TABLE II

INFLUENCE OF STAINLESS-STEEL SAMPLING PROBE

Run No.	Probe material	Combustion conditions	Total nitrogen oxides, p.p.m.
1	Stainless steel	Oxidising	140
	Silica		139
2	Stainless steel		166
	Silica		171
3	Stainless steel	Reducing	3·6
	Silica		58
4	Stainless steel		0·1
	Silica		69
5	Stainless steel		0·3
	Silica		50
6	Stainless steel		2·5
	Silica		51
7	Stainless steel		0·3
	Silica		55
8	Stainless steel		3·9
9	Stainless steel		0·5
10	Stainless steel		0·8
11	Stainless steel		0·1
12	Silica		70
13	Silica		70

It is concluded from this work that stainless-steel probes are not satisfactory for sampling reducing combustion products before the determination of nitrogen oxides. Silica probes, on the other hand, appear to be satisfactory and it is suggested, therefore, that probes of silica or with a silica lining be used for sampling nitrogen oxides in combustion gases containing reducing products.

As it is clearly desirable to use a uniform technique for all sampling it is suggested that when a range of analyses under both fuel-rich and fuel-lean conditions is to be made all measurements should be carried out with the aid of silica or silica-lined sampling probes and with fast sampling flows.

CONCLUSIONS

The Saltzman colorimetric method can be used for rapid and accurate determination of nitrogen dioxide in flue gases from natural gas combustion systems. The calibration factor of 0·72, as determined by Saltzman, has been substantiated. Nitric oxide can be determined by the Saltzman method if it is oxidised to nitrogen dioxide with a sodium dichromate - sulphuric acid oxidation system.

The accuracy of the determination of both nitric oxide and nitrogen dioxide is within approximately ± 5 per cent. of the amount present.

Flue-gas streams must be sampled rapidly through silica or silica-lined probes to prevent oxidation or reduction reactions and thus enable a representative sample to be taken.

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The Determination of Nitric Oxide and Nitrogen Dioxide in Flue Gases

Part II. Continuous Instrumental Methods

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Continuous instrumental methods based on non-dispersive infrared spectroscopy and on coulometry have been evaluated for the determination of nitric oxide and nitrogen dioxide. Instrument modifications have been made when necessary to increase sensitivity in the 0 to 100 p.p.m. concentration range. The interference caused by the presence of other components of the flue gas has been investigated.

Part I[1] of this paper described the analysis of flue gases to determine nitric oxide and nitrogen dioxide (NO_x) by using the Saltzman colorimetric method, together with procedures for sampling the flue gases and preparing pure calibration gases. Although the colorimetric method for determining NO_x has been found to be reliable, a continuously recording instrumental method has obvious advantages for long-term studies. The instrumental techniques that have been reported for the determination of nitric oxide include mass spectrometry,[2] infrared spectroscopy[3] and ultraviolet spectroscopy; this last technique is used after the oxidation of nitric oxide to nitrogen dioxide.[4]

The application of mass spectrometry is limited by the complexity of the equipment and also by difficulties in interpretation for high-temperature systems in which several species with the same mass number as nitric oxide may be present. Ultraviolet spectroscopy can be applied to the determination of nitric oxide only after an oxidation step, and consequently this approach was not favoured because the maintenance of high oxidation efficiencies on a continuous basis is difficult. Infrared spectroscopy was considered to be the most attractive technique for the continuous determination of nitric oxide. The portable non-dispersive gas analysers now commercially available are particularly suitable for this purpose.

Of the methods available for continuously monitoring nitrogen dioxide, ultraviolet spectroscopy does not normally provide sufficient sensitivity. A coulometric technique was therefore investigated.

Determination of nitric oxide by non-dispersive infrared spectrometry

The technique of non-dispersive infrared spectrometry is used extensively for continuously monitoring a single gas component, and the instrumentation required is both simple and robust. A double beam of radiation from a heated Nichrome source is modulated by a rotating chopper before passing simultaneously through reference and sample tubes. The transmitted radiations pass into two detector compartments separated by a thin metal diaphragm, which, together with an insulated plate, forms an electrical condenser. Selectivity is achieved with filters and by filling the detector with the gas to be analysed.

The output is initially balanced with air in the sample tube. When sample gas is introduced, radiation is absorbed in the sample tube and a differential heating effect, and consequent pressure difference, is produced across the detector diaphragm. The resulting electrical signal is amplified, rectified and recorded. Additional selectivity can be achieved by placing gas-filled tubes in the incident light beam. The authors have used the Grubb-Parsons infrared analyser, Model SB2, which incorporates the above principles.

Most industrial non-dispersive infrared nitric oxide analysers have been used for the determination of nitric oxide in automotive exhaust gases and are, therefore, designed to cover concentrations up to 2000 or 3000 p.p.m. of nitric oxide. Flue gases from other sources may contain much lower concentrations of nitric oxide; 50 p.p.m. or less is common. The instrument used had the necessary basic sensitivity for this level, of which use could be

made after the addition of a fine zero control. With the highest sensitivity range provided (0 to 200 p.p.m. of nitric oxide), the base-line noise level was 1 to 2 per cent. of full-scale deflection (f.s.d.). The lower limit of detection was 5 p.p.m. of nitric oxide. Slight variations in temperature and zero gas composition gave rise to a small base-line drift, which usually amounted to less than 4 per cent. of f.s.d. per hour at the highest sensitivity, which was considered acceptable if the zero adjustment was checked regularly. At high sensitivities the response of the detector was affected by the presence of the other constituents of the sample gas. The influence of these constituents was therefore studied.

EFFECT OF WATER VAPOUR—

The maximum absorption of energy for nitric oxide occurs in the region 5·1 to 5·7 μm, whereas water absorbs less strongly in a continuous series of bands from 5·0 to 7·7 μm. Therefore, when the concentration of water is higher than that of nitric oxide serious interference will occur with non-dispersive instruments. In order to overcome this problem a three-stage drying system was devised, which reduced the water content of flue samples to low, insignificant, steady values without loss of nitric oxide.

The bulk of the water was removed from the total sample flow (6 to 7 l min^{-1}) by passage through a simple trap that consisted of a vessel 20 cm × 4 cm diameter immersed in cold water. A flow of 2 l min^{-1} was then led from this main stream through a cooled, 6-m × 6-mm diameter, stainless-steel tube maintained just above 0 °C by a refrigerated bath. By maintaining the temperature of the coil above the freezing-point of the condensate, blockage was prevented during prolonged use. The final drying stage consisted of a double glass trap containing a little glass-wool, which was immersed in a Dewar flask containing solid carbon dioxide. The dry sample was then passed through a pipe to the analysis cell, thermal equilibrium being attained before it reached the cell. The entire drying system was housed within the instrument case.

Table I shows the results of experiments with wet and dry standard gas blends prepared as described under Calibration by using dry or water-saturated nitrogen and dry nitric oxide. These results indicate that no losses of nitric oxide occur with this drying system. The instrument zero must, of course, be adjusted by using air, free from nitric oxide and dried by the above method, as reference gas. In addition to removing water vapour from flue gas samples, the solid carbon dioxide traps also remove nitrogen dioxide and sulphur dioxide. While these two gases have been shown to give only a small response, their removal prevents the possible corrosion of the optical system.

Although the use of solid carbon dioxide is preferred for the final drying stage on grounds of efficiency, ease of handling and removal of corrosive gases, a more readily available drying agent may be advantageous for field work. Of the chemical desiccants examined calcium sulphate is the least active, both chemically and physically, in promoting reaction between flue gas components. Experiments have been carried out in which dry and water-saturated blends were passed through the gas analyser, and substituting calcium sulphate, in the form of self-indicating Drierite, for the solid carbon dioxide trap. The results of these experiments are also shown in Table I.

The above results show that nitric oxide is not lost when dried with calcium sulphate, either by absorption or by promotion of oxidation in the presence of air. The instrument zero was obtained by using air that had been dried under the same conditions.

TABLE I

EFFECT OF DRYING MOIST NITRIC OXIDE BLENDS

Diluent gas	Concentration of nitric oxide in dry gas, p.p.m.	Concentration of nitric oxide, p.p.m., in wetted gas dried with—	
		solid carbon dioxide	calcium sulphate
Nitrogen	199	201	—
Nitrogen	173	176	—
Nitrogen	164	162	—
Nitrogen	150	150	—
Nitrogen	1030	—	1020
Air	820	—	815
Nitrogen	135	—	126
Nitrogen	49	—	49

EFFECT OF OTHER GASES—

Apart from water, nitrogen dioxide and sulphur dioxide, the only common components of flue gas that could give rise to erroneous results for nitric oxide are carbon dioxide and carbon monoxide. The combustion of methane under stoicheiometric conditions produces a flue gas containing about 12 per cent. v/v of carbon dioxide calculated on a dry gas basis.

Blends of carbon dioxide in nitrogen were passed through the infrared gas analyser and modified drying system, and the response was measured. Fig. 1 shows this response expressed in equivalent concentrations of nitric oxide. A correction for the effect of carbon dioxide can thus be made to the indicated nitric oxide concentrations. Infrared absorption results for carbon monoxide suggest that the instrument response for this gas should be less than 10 per cent. of that for carbon dioxide, and this was shown to be so with carbon monoxide blends. As the concentration of carbon monoxide encountered in normal flue gases is usually less than 1 per cent. v/v, its influence is negligible.

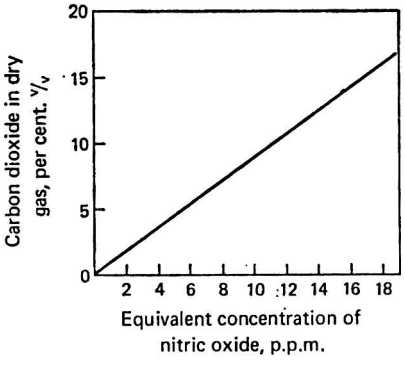

Fig. 1. Effect of carbon dioxide on nitric oxide reading

CALIBRATION—

The infrared gas analyser was calibrated with blends of known composition prepared by diluting a flow of pure nitric oxide or nitric oxide - nitrogen master blends with nitrogen. The two gas flows were accurately measured, by using soap-film flow meters under constant pressure, and thoroughly mixed before being passed into the instrument. The nitric oxide concentration was calculated from the flow-rates and also determined by the colorimetric technique described in Part I of this paper. In general, the calculated and determined values agreed closely, as shown in the typical calibration graphs (Figs. 2 and 3). These graphs cover the ranges 0 to 200 and 0 to 2000 p.p.m. of nitric oxide; further calibration graphs have been constructed for intermediate ranges.

DETERMINATION OF NITROGEN DIOXIDE BY COULOMETRY

Results obtained by the colorimetric procedure described in Part I showed that concentrations of nitrogen dioxide are less than 10 p.p.m. in many combustion systems. The need for high sensitivity, continuous monitoring and rapid response suggested that the coulometric instrument first described by Mast[5] should be evaluated. The principle upon which this instrument is based was first applied to the determination of ozone but has more recently been applied to the measurement of low nitrogen dioxide concentrations.[6–8] The sensor of this instrument consists of two platinum electrodes over which flows a buffered iodide solution. A small potential applied to these electrodes causes polarisation to occur, and no current flows. The reaction of a small proportion of the nitrogen dioxide passing over the iodide solution causes depolarisation and the subsequent polarising current is proportional to the nitrogen dioxide concentration.

An instrument involving the use of this technique, the Mast, Model 724–11, nitrogen dioxide analyser, was used for the work described.

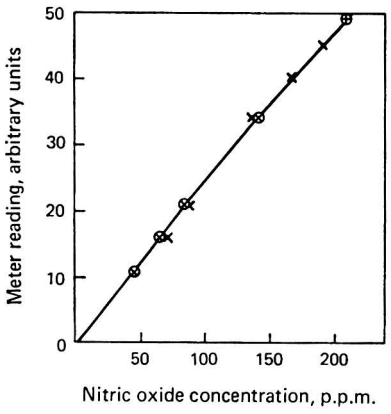

Fig. 2. Nitric oxide calibration range 6. ×, concentration by flow measurement; and o, concentration by Saltzman determination

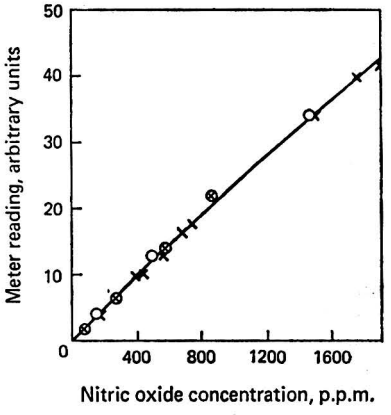

Fig. 3. Nitric oxide calibration range 3. ×, concentration by flow measurement; and o, concentration by Saltzman determination

SENSITIVITY—

The sensitivity of the above technique is a function of solution composition and, to a lesser extent, solution flow-rate and gas sample flow-rate. The latter parameters are normally held constant, typical flows being 2·5 ml h^{-1} of solution and 140 ml min^{-1} of sample gas. The highest instrument sensitivity is obtained by using a phosphate-buffered solution containing potassium iodide and bromide, with monoethylene glycol added as a wetting agent. The sensitivity was found to depend on the iodide concentration. This latter parameter was varied to give three sensitivity ranges, 1 per cent. w/w of iodide giving f.s.d. with about 11 p.p.m. of nitrogen dioxide while 0·2 and 0·05 per cent. gave f.s.d. with about 30 and 110 p.p.m., respectively.

To measure higher concentrations of nitrogen dioxide a solution containing potassium bromide and citric acid was used. Less variation in sensitivity was attained by using this type of solution, but increasing the bromide concentration from the original 5 to 10 per cent. w/w provided a linear calibration with f.s.d. corresponding to about 670 p.p.m. of nitrogen dioxide.

EFFECT OF MOISTURE—

It was observed that the presence of water vapour in nitrogen dioxide blends suppressed the instrument response when using an iodide-based solution. This effect was investigated by maintaining the water concentration of various nitrogen dioxide blends constant by first mixing a nitrogen flow saturated with water at elevated temperatures with nitrogen dioxide and then equilibrating at ambient temperature in the presence of the condensate formed. This process roughly simulated the conditions existing in sample probes. To ensure that the reduction in sensitivity was not caused by loss of nitrogen dioxide by reaction with water, the moist blends were analysed for nitrogen dioxide by the colorimetric procedure previously described. Some typical results are shown in Table II.

TABLE II

EFFECT OF WATER VAPOUR ON THE NITROGEN DIOXIDE CONTENT OF BLENDS

Temperature of saturation/°C	Temperature of final equilibration/°C	Nitrogen dioxide concentration of dry gas, p.p.m.	Nitrogen dioxide concentration of wet gas, p.p.m.
23	23	60	59
60	23	60	58
100	23	60	57
100	23	8	8

These results show that over the range investigated nitrogen dioxide is not lost from moist blends to any appreciable extent. The reduction in sensitivity of the coulometric instrument in the presence of water vapour is shown in Fig. 4.

EFFECT OF NITRIC OXIDE—

Although it has been shown that the instrument does not respond to nitric oxide, it was found that this gas suppressed the response to nitrogen dioxide in a manner similar to the suppression caused by water vapour.

CALIBRATION—

The instrument was calibrated by diluting previously analysed nitrogen dioxide - nitrogen master blends with nitrogen. The final nitrogen dioxide concentration was also determined by the colorimetric procedure. As water vapour and nitric oxide are always present in flue gases, usually at higher concentrations than nitrogen dioxide, calibrations were carried out in the presence of both. A typical curve is shown in Fig. 4. The water concentration was held constant at ambient temperature and the nitric oxide concentration at two arbitrary levels. The curves show that to obtain accurate results for nitrogen dioxide, the nitric oxide content must also be known and the water content equilibrated at ambient temperature

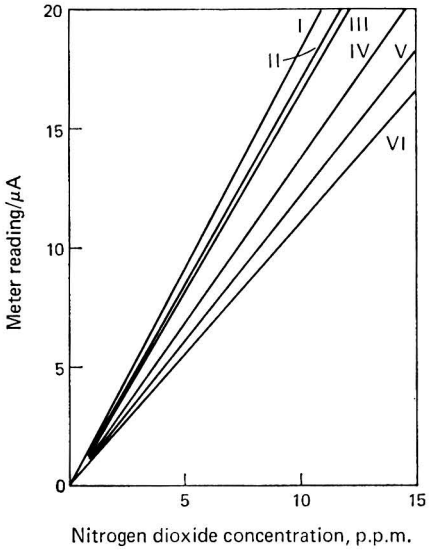

Fig. 4. Coulometric determination of nitrogen dioxide (calibration by using 1 per cent. w/v potassium iodide solution). I, Dry gas; II, dry gas + 50 p.p.m. of NO; III, dry gas + 150 p.p.m. of NO; IV, gas saturated with water at 25 °C; V, gas saturated with water at 25 °C + 50 p.p.m. of NO; and VI, gas saturated with water at 25 °C + 150 p.p.m. of NO

CONCLUSION

Non-dispersive infrared techniques are ideally suited to the continuous monitoring of nitric oxide in flue gases. Commercial gas analysers are available which, with minor modifications, can operate in the range 0 to 200 p.p.m. with a lower limit of detection of 5 p.p.m. Water vapour is the major interfering flue gas component but can be removed with solid carbon dioxide cooled traps or with calcium sulphate without loss of nitric oxide.

Nitrogen dioxide can be continuously determined by the coulometric technique described by Mast. The sensitivity is affected by water vapour and nitric oxide, and calibration in the presence of these gases is essential.

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NOTE—Reference 1 is to Part I of this series.

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Potentiometric and Spectrophotometric Methods for the Determination of Bisthiosemicarbazones

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A method has been developed for the quantitative determination of bisthiosemicarbazones in which addition of copper(II) chloride to a solution of the organic compound leads to complex formation. The hydrogen ions liberated on complex formation are determined by potentiometric titration. The complex, or the organic ligand itself, can also be determined spectrophotometrically.

Bisthiosemicarbazones with alkyl side-chains are compounds of interest because of their potential use as pharmacological agents against cancer,[1] protozoa[2] and fungi.[3] During our investigation of metal complexes of these compounds (unpublished results) we observed that no reliable method for the quantitative determination of these organic compounds was available. Koshkin's method,[4] which is time-consuming as it involves precipitation, filtration and back-titration, and is also unreliable because it has an indefinite end-point, suffers from the disadvantage that with bisthiosemicarbazones with side-chains containing ester groups, breakdown of the molecule as a result of hydrolysis may occur, thus giving rise to erroneous results. Petering and van Giessen[5] in their work on 3-ethoxy-2-oxobutanal bisthiosemicarbazone reported that the liberation of hydrogen ions on complex formation of the ligand with copper(II) chloride was almost quantitative.

In this paper we outline simple and rapid methods for the quantitative determination of bisthiosemicarbazones. The first method is by potentiometric titration of the hydrogen ions liberated on complex formation when copper ions are added to a solution of the organic compound. The method is similar to that recently developed for monothiosemicarbazones.[6] The second method consists in spectrophotometric determination of either the organic compound or the complex formed on addition of copper(II) chloride to the bisthiosemicarbazone.

Experimental

Potentiometric method—

The apparatus used was as described previously.[6] The reagents used were 0·1 M sodium hydroxide (as the standard base) and a 2 per cent. w/v aqueous solution of copper(II) chloride dihydrate.

Weigh accurately about 100 mg of bisthiosemicarbazone and dissolve it completely in 90 ml of dioxan contained in a beaker. Add 20 ml of water and 5 ml of the copper(II) chloride solution. Stir the mixture with a magnetic stirrer and titrate it with the standard base. A typical set of titration figures, which were obtained with a Vibret pH meter and used for manual plotting of a graph, is given below.

Titrant added/ml	0·0	5·2	5·4	5·5	5·6	5·7	5·8	5·9	6·0	6·1	6·2	6·4	6·6
pH reading	1·90	2·80	2·90	3·01	3·14	3·30	3·60	4·22	4·50	4·70	4·83	4·90	4·94

Determine a blank under the same experimental conditions (the value found was about 0·02 ml of titrant).

The percentage purity is easily calculated from the equation—

$$\text{Percentage purity} = \frac{V \times N \times E}{W \times 10}$$

where V is the volume of titrant in millilitres corrected for the blank; N is the normality of titrant; E is the equivalent weight of organic compound in grams (equal to half the molecular weight); and W is the weight taken in grams.

SPECTROPHOTOMETRIC METHOD—

A Unicam SP800 double-beam recording spectrophotometer was used for the determination of peak maxima and a Unicam SP500 single-beam manual instrument for the accurate determination of absorbances. The procedures described below give the average value for the molar absorptivity, and also serve to show the limits of the method.

The same stock solutions, which were prepared by accurately weighing between 34 and 36 mg (see Table I) of 3-butyryloxy-2-oxobutanal bisthiosemicarbazone and dissolving the samples in methanol, the volume being made up to 100 ml, in calibrated flasks, were used for determinations of both the organic compound and its copper complex.

TABLE I

SPECTROPHOTOMETRIC DETERMINATION

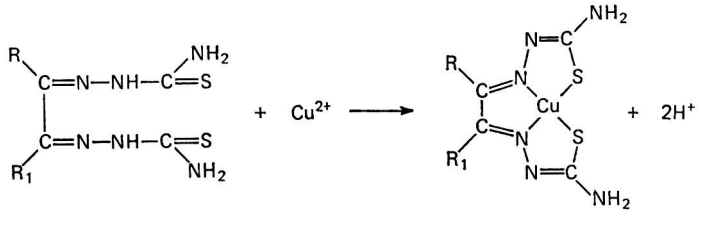
	Organic compound		Copper complex	
Weight of substance/mg	Mean reading ($\times 10^3$)	ϵ	Mean reading ($\times 10^3$)	ϵ
34·01	407	38 110	442	5170
34·24	407	37 850	447	5197
34·49	409	37 760	453	5227
34·72	412	37 780	455	5216
35·00	421	38 300	456	5186
35·22	421	38 060	463	5231
35·43	424	38 100	459	5156
35·74	428	38 120	470	5234
35·97	434	38 410	475	5254
	σ = 0·58 per cent.		σ = 0·66 per cent.	
	$\epsilon_{average}$ = 38 230		$\epsilon_{average}$ = 5240	

For direct determinations of absorbance on the organic compound dilute 1 ml of each stock solution to 100 ml in a calibrated flask and determine the absorbance at the peak maximum against a methanol blank in 1-cm cells.

For determinations on the copper complex of the organic compound, introduce, with a pipette, 4 ml of stock solution into a 50-ml calibrated flask, add 5 ml of aqueous 0·04 per cent. w/v copper(II) chloride solution and make the volume up to the mark with methanol. Determine the absorbances at the peak maximum against a blank solution of 5 ml of copper solution made up to 50 ml with methanol. The results for 3-butyryloxy-2-oxobutanal bisthiosemicarbazone are given in Table I and the compounds studied are shown in Table II.

RESULTS AND DISCUSSION

Addition of copper(II) chloride to the bisthiosemicarbazone leads to complex formation, in which two equivalents of hydrogen ion are released into solution—



The structure of a complex of this type has been reported previously.[7]

The determinations were carried out potentiometrically on ten different samples for each bisthiosemicarbazone and the results obtained were within the narrow range of 100 ± 0·5 per cent. The method was successful with the bisthiosemicarbazones of the following compounds: heptan-2,3-dione, 4-phenylbutan-2,3-dione, 3-ethoxy-2-oxobutanal, 3-propoxy-2-oxobutanal, 3-propionyloxy-2-oxobutanal, 3-butyryloxy-2-oxobutanal and 3-valeryloxy-2-oxobutanal.

A satisfactory end-point could be obtained even for amounts as small as 20 mg, but the scatter of results increased to ±2 per cent., probably because of the inaccuracy in burette readings. In an attempt to decrease this scatter, weaker solutions of the alkali standard were used, but as this resulted in a more poorly defined titration curve and a less accurately determined end-point, dilution of the titrant had no advantage.

Erroneous results can be caused by too great a concentration of the complex in the solution, resulting in the precipitation of solid complex. With an automatic titrator a concentration of 100 mg of the organic compound in 20 ml of dioxan *plus* 25 ml of water gave satisfactory results but greater dilution had to be used with the manual method.

In the spectrophotometric method the dilutions required are such that the Beer - Lambert law is obeyed. The high molar absorptivity obtained for the organic compound requires high dilution, and therefore accuracy in weighing and in the use of pipettes is needed. Under the experimental conditions used the results were within the narrow range of 100 ± 0·9 per cent. (coefficient of variation 0·58 per cent.).

The decrease in the molar absorptivity on complex formation leads to smaller dilutions being required and therefore to less demanding techniques of weighing and in the use of pipettes. However, there is a slight shift in the band maximum with the change in the amount of water present and therefore additional care must be taken during the measurements. The shifts are particularly large for oxobutanal compounds. The results obtained were within the range of 100 ± 1·3 per cent. (coefficient of variation 0·66 per cent.).

TABLE II

MOLAR ABSORPTIVITIES OF THE BISTHIOSEMICARBAZONES AND THEIR COPPER COMPLEXES

Ligand	Ligand		Copper complex	
Bisthiosemicarbazones	$\lambda_{max.}$/nm	ϵ	$\lambda_{max.}$/nm	ϵ
Heptan-2,3-dione	329	49 000	470	5300
4-Phenylbutan-2,3-dione	330	39 300	472	4860
3-Propionyloxy-2-oxobutanal	345	38 700	480	4820
3-Butyryloxy-2-oxobutanal	345	38 500	481	4940
3-Valeryloxy-2-oxobutanal	345	38 900	481	5090
3-Ethoxy-2-oxobutanal	347	47 200	483	6380
3-Propoxy-2-oxobutanal	347	44 900	483	6180
Thiosemicarbazide	241	11 800	—	—

EFFECT OF IMPURITIES—

The main impurity that may occur in the preparation of the compounds studied is thiosemicarbazide, which is used in the final condensation stage. To ascertain its effect, thiosemicarbazide was added to pure 3-butyryloxy-2-oxobutanal and measurements of the ligand gave the following results—

	Spectrophotometric						Potentiometric		
Pure ligand in sample, per cent.	100·00	99·62	99·07	98·41	97·98	97·56	99·5	99·0	98·5
Purity found experimentally, per cent.	99·83	99·67	99·40	98·84	98·00	97·12	101·3	101·5	102·1

The percentage purity can easily be determined spectrophotometrically and the mean of several determinations gives the approximate amount of the pure material present in the sample. The absorption of thiosemicarbazide at the $\lambda_{max.}$ of measurement for bisthiosemicarbazones is almost zero. In the potentiometric method a higher percentage is obtained because under the experimental conditions used the thiosemicarbazide forms an inner complex with copper salts, with subsequent release of hydrogen ions. Because of the difference in molecular weight between bisthiosemicarbazones and two molecules of thiosemicarbazide the results are high.

The following comments can be made on the usefulness of the methods.

(*i*) For the range of amounts used (30 to 60 mg) the potentiometric method gives results with a smaller standard deviation than the spectrophotometric method, although the latter will obviously yield more accurate results if much smaller amounts of samples are available. However, the experimental conditions, *e.g.*, solvent concentration, are less stringent in the potentiometric method.

(*ii*) The time required to perform a determination is comparable for both methods, but the apparatus used in the potentiometric method is less costly and probably more readily available.

(*iii*) In the spectrophotometric method no advantage is gained by the use of complex formation instead of pure ligands.

(*iv*) Both methods have advantages over Koshkin's procedure in that they are rapid, even when using manual apparatus, the end-point or absorbance, according to which method is used, is easier to determine, and no hydrolysis has been observed under the experimental conditions described above.

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The Microbiological Assay of Total and Free Inositol with *Schizosaccharomyces pombe*

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Improvements are suggested in basal medium and in methods of hydrolysis for the microbiological assay of inositol with a strain of *Schizosaccharomyces pombe*.

It has been tentatively suggested by Emery, McLeod and Robinson[1] that either of the yeasts *Kloeckera brevis* and *Schizosaccharomyces pombe* might prove to be a suitable organism for the microbiological assay of inositol. Northam and Norris[2] explored these possibilities further and came to the conclusion that *Schizosaccharomyces pombe* was to be preferred to *Kloeckera brevis*, mainly on the ground that lower concentrations of inositol were required to establish a standard curve, and therefore the possible presence of interfering substances in the test solution would be correspondingly reduced. They also introduced several improvements in the basal medium devised by Emery *et al.*[1] Later, Norris and Darbre[3] described how this organism can be used for the routine assay of inositol, with the same basal medium as that used by Northam and Norris.

The author has found that although the procedure of Norris and Darbre gives good results it has the disadvantage that it requires the use of an inositol-free yeast supplement, which is difficult and tedious to prepare. It was later discovered that the vitamin additions, especially biotin, recommended by Norris and Darbre, are sub-optimal for this organism and the addition of the yeast extract supplement merely brought these sub-optimal amounts to the requisite levels. If the vitamin levels are increased to the concentrations recommended here, the addition of the yeast supplement will be found to be unnecessary.

It was also found that the inorganic salt solution recommended by Emery *et al.*, and since used by other investigators, can be replaced by the simpler inorganic solution devised by the author.[4]

The nitrogen requirements of *Schizosaccharomyces pombe* appear to be simple and the organism grows vigorously with ammonium sulphate as the sole source of nitrogen. The finding of Northam and Norris[2] that the addition of asparagine[1] is unnecessary was confirmed. It was also found that vitamin-free casein hydrolysate is inferior to ammonium sulphate as the sole source of nitrogen.

The level of glucose in the basal medium was maintained at 2 per cent., as recommended by Emery *et al.* Increasing the level to 4 per cent., as suggested by Norris and Darbre, led to more vigorous fermentation but there was no increase in the growth of the organism.

The lactate buffer used by Norris and Darbre has been replaced with potassium citrate and citric acid.[4]

Experimental

Maintenance of organism—

The strain of *Schizosaccharomyces pombe* used in this investigation is not the same as that used by Norris and Darbre, but is one that has been included in our laboratory collection for many years.

The organism is maintained in liquid stock culture in exactly the same way as described by the author for *Kloeckera brevis*[4] and on the same malt - yeast - glucose medium.

BASAL MEDIUM—

The inositol-free basal medium (5×strength) has the following composition—

Ammonium sulphate	2·0 g	Niacin (nicotinic acid)	5000 μg
Potassium dihydrogen orthophosphate	0·6 g	Calcium *d*-pantothenate	5000 μg
Tripotassium citrate	5·0 g	Thiamine hydrochloride	5000 μg
Citric acid	1·0 g	Pyridoxine hydrochloride	5000 μg
Potassium chloride	0·5 g	Biotin	40 μg
Calcium chloride (anhydrous)	0·2 g	Inorganic salt solution (see below)	6·3 ml
		Water to	100 ml

After mixing, the pH of the medium is adjusted to 5·0 either electrometrically or by using bromocresol green as external indicator, and the solution is stored at a temperature not exceeding 4 °C and used within 7 days. Immediately before an assay, the solution is gently warmed, 20 g of glucose are added and the total volume is made up to 200 ml with water.

Inorganic salt solution—Ten grams of magnesium sulphate ($MgSO_4.7H_2O$), 0·5 g of manganese(II) sulphate ($MnSO_4.4H_2O$) and 0·1 g of anhydrous iron(III) chloride are dissolved in 250 ml of water and 5 drops of concentrated hydrochloric acid added. This solution will maintain its activity indefinitely at room temperature.

ASSAY PROCEDURE—

It is essential to establish a separate standard curve for each assay. The amounts of inositol required to establish such a curve are 0·00, 0·5, 1·0, 1·5, 2·0 and 2·5 μg. A solution of inositol containing 1·0 μg ml^{-1} is prepared and of this standard solution the following amounts are used to establish the range of standards: blank (4 ml of water); 0·5 ml of standard solution *plus* 3·5 ml of water; 1·0 ml of standard solution *plus* 3·0 ml of water; 1·5 ml of standard solution *plus* 2·5 ml of water; 2·0 ml of standard solution *plus* 2·0 ml of water; and 2·5 ml of standard solution *plus* 1·5 ml of water. The volume of liquid in each of the tubes is adjusted to 5 ml by the addition of 1·0 ml of basal medium, and a glass bead is placed in each tube.

Test preparations are set up at three concentrations by taking either 0·5, 1·0 and 2·0 ml or 1·0, 2·0 and 4·0 ml of the test extract, depending upon the expected potency of the test material, making the volume up to 4 ml with water and adding 1 ml of basal medium.

The water and basal medium are added to each tube with a 5-ml calibrated B-D Cornwall Luer-Lok syringe and the standard and test solutions with a 2-ml calibrated instrument.

All concentration levels of standard and test solutions are prepared in triplicate. The tubes are capped with aluminium thimbles, with coloured thimbles for the blanks, sterilised by steaming for 15 minutes, cooled and inoculated.

PREPARATION OF INOCULUM—

About 10 ml of a 24-hour-old liquid stock culture is aseptically centrifuged, the deposit is washed once on the centrifuge with sterile distilled water and then suspended in 10 ml of sterile distilled water. One drop of this suspension is added to each tube, but omitting, however, to inoculate one of the blanks so as to set the colorimeter.

The tubes are incubated on a shaker at 25 ± 1·0 °C for 72 hours. After incubation, 5 ml of water are added to each tube, the mixture is steamed for 15 minutes and the response is determined nephelometrically.

PREPARATION OF SAMPLES—

Free inositol—The method described by Norris and Darbre for the determination of free inositol[3,5] gave excellent and reproducible results and can be recommended.

Total inositol—The author has found that the best method of extracting total inositol by hydrolysis with hydrochloric acid depends on the nature of the material. Norris and Darbre heated 100 to 200 mg of material with 2 ml of N hydrochloric acid in a sealed Pyrex tube for 48 hours at 123 °C. This method is unsuitable and presents practical difficulties in routine work.

It was found that hydrolysis with N hydrochloric acid was superior to hydrolysis with either 3 or 4 N acid as has been recommended in the past; the use of the more concentrated acids with materials such as black strap or beet molasses may destroy up to 60 per cent. of

the inositol. Hydrolysis of 100 to 200 mg of molasses with 2 ml of N hydrochloric acid at 15 p.s.i. for 30 minutes appeared to release the whole of the bound inositol and hydrolysis for longer periods (4 to 10 hours) led to no further increase; in fact, after 10 hours some of the inositol was destroyed.

The following method has now been adopted as standard procedure in this laboratory. For all material, other than molasses, 100 to 200-mg amounts are accurately weighed into Pyrex tubes and hydrolysed with N hydrochloric acid for 10 hours at 15 p.s.i. After hydrolysis, the tubes are cooled and the contents washed into a calibrated flask, the pH is adjusted to between 4·8 and 5·0, with bromocresol green as external indicator, and the contents are made up to volume and filtered. Further dilution may be necessary, depending upon the inositol content of the material.

CALCULATION—

For normal routine work in the laboratory direct reading from the standard curve will be found to be adequate, provided that there is no regular drift in the values at the different concentration levels and that the levels do not differ among themselves by more than ± 10 per cent. A more accurate assessment can be made with the Wood[6] "log - log" procedure. If fiducial limits are required they should be calculated by computer.

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Communications

Material for publication as a Communication must be on an urgent matter and be of obvious scientific importance. Manuscripts must not exceed 300 words; rapidity of publication precludes the use of diagrams, but tables or formulae may be included if the length of text is reduced appropriately. Communications should not be simple claims for priority. This facility for rapid publication is intended for brief descriptions of work that has progressed to a stage at which it is likely to be valuable to workers faced with similar problems. A fuller paper may be offered subsequently, if justified by later work.

Manuscripts are *not* subjected to the usual examination by referees. Inclusion of a Communication is at the Editor's discretion; a manuscript not accepted as a Communication may, if the author wishes, be re-submitted as a possible paper and subjected to the usual scrutiny by referees.

A NEW GRAPHITE ROD FOR FLAMELESS ATOMIC-ABSORPTION SPECTROSCOPY

WEST and co-workers[1,2] have described a graphite rod (filament) that provides a reservoir for atomic absorption and atomic fluorescence. The solution (1 to 5 μl) is supported on a flat surface at the centre of the rod. A similar rod having a circular cavity for the solution was used by Amos, Bennett, Brodie, Lung and Matousek.[3]

We have improved the limit of detection by designing, specifically for atomic absorption, a rod that can contain a larger volume of solution (50 μl) and provides a longer path for the radiation through the cloud of atoms.

This rod, the NIM rod, is made of Ringsdorff RWO graphite, is 4·5 mm in diameter and 66 mm long, and fits the workhead of the Varian Techtron Carbon Rod Analyser. A slot 1·9 mm wide, 1·5 mm deep and 20 mm long is machined in the top of the rod. To ensure uniform heating, the rod is machined down to a diameter of 3·1 mm over two 5-mm sections extending for 16 to 21 mm from each end. The workhead of the analyser is turned parallel to the light path so that the longitudinal axis of the rod is in the optic axis.

Detection limits for a signal-to-noise ratio of 2 for gold, measured on a Varian Techtron AA5 instrument, were 0·0005 p.p.m. with the NIM rod, 0·005 p.p.m. with the Varian Techtron rod (5-μl cavity) and 0·01 p.p.m. with an air - acetylene flame, thus showing the substantial improvement obtained by using the NIM rod.

We thank the Director of the National Institute for Metallurgy for permission to publish this communication.

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THE DETERMINATION OF LEAD IN BIOLOGICAL MATERIALS BY HIGH-ENERGY γ-PHOTON ACTIVATION

RECENT concern about the detrimental effects of pollution has restimulated interest in the determination of heavy metals, such as lead, in biological materials. Activation methods offer a number of advantages, including freedom from reagent blank, over conventional analytical techniques but have not been widely applied to this field. The most sensitive neutron-activation procedure for the determination of lead involves the use of the $^{208}Pb(n,\gamma)^{209}Pb$ reaction but the short half-life (3·3 hours) and β^--decay of ^{209}Pb necessitates its rapid and specific radiochemical separation from the highly active matrix.

High-energy γ-photon activation, on the other hand, produces radionuclides from lead that decay with diagnostic γ-ray emission, as shown in Table I.

TABLE I

LEAD RADIONUCLIDES PRODUCED BY γ-ACTIVATION

Target nuclide	Reaction	Product nuclide	Half-life	γ-Emission/keV
^{204}Pb	γ,n	^{203}Pb	52·1 h	279 (81%), 401 (5%), 680 (1%)
^{206}Pb	γ,2n	^{204m}Pb	67 min	375 (93%), 900 (189%, doublet)
^{204}Pb	γ,γ'			

We have investigated the use of this technique for the determination of lead in biological materials. To obtain optimum sensitivity, a radiochemical procedure for the separation of ^{203}Pb has been adopted. Our previous work[1] on the non-destructive analysis of rock and biological materials following γ-activation has shown that, for calcium-rich matrices (as for those used in this study) the $^{44}Ca(\gamma,p)^{43}K$ and $^{48}Ca(\gamma,n)^{47}Ca$ reactions produce the majority of the activity from which the ^{203}Pb or ^{204}Pb is required to be separated.

Samples and suitable standards are irradiated for 2 hours in the bremsstrahlung produced from 5 μA (measured on the 3-mm tungsten converter) of 35 to 40 MeV electrons by using the Harwell Linac. To date, three biological materials have been studied. The results obtained are shown in Table II together with results of independent analytical techniques on portions of the same samples.

TABLE II

DESTRUCTIVE DETERMINATION OF LEAD IN BIOLOGICAL MATERIAL

Matrix	Amount found, p.p.m. γ-Activation	Amount found, p.p.m. Other methods
Kale (dry wt.)	2·7 ± 0·4 (8 determinations)	3·2 (1·6 to 5·4) (ref. 2)
Orchard leaves (dry wt.)	42 ± 2 (6 determinations)	44 (ref. 3)
Human bone (ash)	15·7 ± 0·7 (4 determinations)	15·5 (4 methods) (ref. 4)

The limit of detection of the technique, based on three standard deviations of the sodium iodide (thallium) detector background at 279 keV and the specific activity of the lead, at a time sufficient to permit radiochemical separation, is approximately 0·1 μg.

An evaluation of the accuracy of the method in the range 5 to 30 p.p.m., involving standard additions of lead to kale, and of the possible effects of interferences, is in progress.

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ANALYTICAL SCIENCES DIVISION,
U.K.A.E.A., RESEARCH GROUP,
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Book Reviews

CIPAC HANDBOOK. VOLUME I. Analysis of Technical and Formulated Pesticides. Compiled by R. ASHWORTH, J. HENRIET and J. F. LOVETT and edited by G. R. RAW. Pp. xvi + 1079. Collaborative International Pesticides Analytical Council Ltd. Cambridge: W. Heffer and Sons Ltd. 1970. Price £10·00.

The methods given in this handbook have been adopted as a result of extensive collaborative analytical laboratory work over a number of years by the Collaborative International Pesticides Analytical Council Ltd. (CIPAC) and its working panels of official and industrial scientists. The aims of the Council, which was formed during the IVth International Congress on Crop Protection at Hamburg in 1957, are to promote international agreement on methods for the analysis of pesticides, for correlating biological efficacy with physical and chemical tests and for evaluating pesticide formulations. To avoid unnecessary duplication CIPAC has worked very closely with the Association of Official and Analytical Chemists (A.O.A.C.), the Food and Agricultural Organisation (F.A.O.) and the World Health Organisation (W.H.O.). Consequently the methods given for the analysis of technical and formulated pesticides in this first edition of the handbook represent internationally agreed analytical procedures collected and tested, on a collaborative basis, through the various Pesticide Analysis Advisory Committees of the member countries. This useful handbook contains a comprehensive selection of analytical procedures and techniques used in evaluating technical and formulated products, and the compilers are to be congratulated on bringing together, in one volume, a wealth of chemical detail and information culled from so many national and international committees for the benefit of formulation chemists.

The book is divided into eight chapters, the first three of which are informative in nature, giving the history of CIPAC, the *modus operandi* and a glossary of clearly defined terms which are used in the experimental procedures. The major part of the handbook (Chapter 4; 700 pages) presents graded methods for the analysis of some sixty pesticides that may be encountered in formulations of various types, *e.g.*, dusts, dispersible powders, emulsifiable concentrates and seed dressings. The formula, correct (I.S.O.) name, physical and chemical constants, compatibility information, etc., are given for each pesticide followed by detailed procedures for the analysis of the active ingredient present in various formulations, and methods for quantitatively assessing formulation parameters, *e.g.*, flowability, storage stability, wettability and suspensibility. The experimental procedures are clear, concise and sufficiently detailed that the handbook may be used as a bench manual by the most inexperienced worker in the field.

This section is followed by a short chapter (12 pages) on the application of infrared spectroscopic techniques to the analysis of both technical-grade pesticides and their formulations with particular reference to their use as a quantitative screening test for pesticide samples. Chapter 6 (88 pages) deals with the preparation, purification and standardisation of the various reagents required in pesticide formulation analysis and includes volumetric (titrimetric) methods. Over seventy reagents are described and again the style is clear, concise and informative.

The various analytical techniques, essential for carrying out the analytical methods given in Chapter 4, are described in great detail in Chapter 7 (200 pages). These techniques (eighty in total) range from determinations of melting-points, through determinations of the volatility of phenoxyacetic acid ester formulations by measuring the effect on selected tomato plants, to particle-size distribution of a DDT dispersible powder and flowability methods for powders. Many other analytical techniques, peculiar to the formulation chemists, are described in ample detail in this section of the handbook.

The final chapter presents methods for preparing and purifying certain technical pesticides (eleven compounds) for use as standards when required. Some of the compounds described are checked for their purity by using thin-layer chromatographic, gas - liquid chromatographic and mass-spectrometric techniques. However, in this chapter, no warning is given of the hazardous nature of many of these pesticides when they are handled in bulk, *e.g.*, "weigh out technical dieldrin (about 300 g)" on p. 1021. In particular, dinoseb and endrin are handled in bulk in the given procedures without any warning of their toxic nature, despite the fact that both these compounds are included in the Agriculture (Poisonous Substances) Regulations as Second Schedule, Part II, substances!

Appendices give the very useful code numbering of the pesticides used throughout the handbook for both the methods of analysis and the specifications used, and also the specification for

precision thermometers. These are followed by an index of Chemical Code Numbers of pesticides in Chapter 4 and by a general index.

It is inevitable in a book of this size, containing such a wealth of chemical information, that a few discrepancies and inconsistencies should slip through the editing process, *e.g.*, the structure of captan (p. 171) is wrongly printed; the determination of water in acetone solutions (p. 902) reads "mix sample (10 ml) with distilled water (190 ml) . . ." but should, of course, read ". . . light petroleum (b.p. 100 to 120 °C; 190 ml)"; the index of Chemical Code Numbers (p. 1049) is arranged numerically from 1 to 89, but 33 intermediate numbers are not allocated. Similarly, although this handbook is a methods manual to be used at the bench, some of the procedures contained therein are duplicated unnecessarily, *e.g.*, the procedure for the determination of the apparent density after compaction without pressure (p. 977) is identical with that given for the tap density determination (p. 908) and could therefore be eliminated by cross-referencing to MT33; the section dealing with loss on drying (pp. 871 to 875) at various temperatures and pressures could be more consistent in the four experimental procedures given (x, y, z and w represent different weighings in each procedure), and is it necessary to quote virtually the same formula for the percentage loss on drying on four successive pages?

Several inconsistencies were found in the book, particularly regarding the status of methods. In the introduction to Chapter 4 (p. 13) the authors state that "CIPAC collaborates closely with the A.O.A.C. and the two organisations adopt each other's methods. This is indicated by a method being designated as CIPAC - A.O.A.C. or A.O.A.C. - CIPAC. The first indicates that the method was developed by CIPAC and adopted by A.O.A.C.; the second, *vice-versa*." This is misleading as the reviewer found 209 CIPAC methods, 22 A.O.A.C. - CIPAC methods, but not a single CIPAC - A.O.A.C. method! One implication is that none of the CIPAC methods has been adopted by the A.O.A.C. Again, the methods given in the book for the analysis of diquat (p. 342) and paraquat salt aqueous formulations (p. 547) are designated as CIPAC methods, but in the Eleventh Edition (1970) of the A.O.A.C. Methods book identical procedures are given for these two formulations (p. 95) and yet are designated as A.O.A.C. - CIPAC methods!

Finally, the authors do not make it clear for whom the handbook is written. Presumably it is aimed at pesticide manufacturers who prepare formulations and therefore require quality control tests, distributors/agencies who purchase active ingredients and prepare the formulations themselves, and various government laboratories, both in Britain and overseas, who would use the methods for testing chemical specifications and controlling the sale of pesticide formulations to the general public and the agricultural community. Consequently, it would seem that the scientists who will purchase copies of this handbook will, in the main, be those scientists who have been involved in its preparation!

Despite the above comments, however, this handbook endeavours to fulfil a real need in formulation chemistry by bringing together and collating in one large volume the many diverse experimental procedures that cover a very wide range of scientific expertise scattered throughout the literature and hidden away in the laboratories of industrial and governmental establishments. The result is a functional handbook which goes far towards standardising the analytical methods and techniques of the pesticide chemist on an international basis. It is hoped that the next edition of the book will be more functional by including more methods based on modern analytical techniques, *e.g.*, thin-layer chromatography, gas - liquid chromatography with its variety of detectors, and atomic-absorption spectrophotometry for metal analysis, which are rapidly becoming the preferred tools of the analytical chemist in the modern analytical laboratory. B. FLAHERTY

ABSORPTION SPECTRA IN THE ULTRAVIOLET AND VISIBLE REGION. Edited by L. LÁNG. VOLUME XIV. Pp. i + 400. 1970. Price £7. VOLUME XV. Pp. i + 408. 1970. Price £7. CUMULATIVE INDEX, VOLUMES XI–XV. Pp. vi + 103. 1971. Price £0·75. Budapest: Akadémiai Kiadó.

Volume XIV follows the established pattern for the series. It includes familiar and unfamiliar derivatives of acetophenone, flavan, flavone and flavanone, of phenol and naphthalene, of pyridine, pyrimidine and of purine, quinazoline and silane (spectra of 187 compounds are shown graphically and tabulated). Volume XV deals *inter alia* with aniline, aminophenol, quinoline and quinoxaline derivatives but it possesses special interest because it includes spectra of a large number of heteroaromatic compounds containing seven-membered rings (oxepin, thiepin, selenepin, methiadene and tarpan derivatives). The useful cumulative index covers the last five volumes.

R. A. MORTON

Notice to Authors

The Editor welcomes papers on all aspects of the theory and practice of analytical chemistry, fundamental and applied, inorganic and organic, including chemical, physical and biological methods. Papers are submitted to referees, who will advise on their suitability for publication.

Intending authors should consult the current Notice to Authors, last published in full in *The Analyst*, **1968**, **93**, 269–272, reprints of which can be obtained on application to The Editor, *The Analyst*, 9/10 Savile Row, London, W1X 1AF.

A Computer Method for the Spectrophotometric Determination of Overlapping pK_a Values

A least-squares computer method has been developed to obtain two pK_a values from spectrophotometric data in instances when the values are so close together that the calculations usually applied for individual pK_a values are not appropriate. A scaling procedure improves the condition of the matrix that is constructed in solving the sets of simultaneous equations. Two examples of applications of the method are given.

G. HEYS, H. KINNS and D. D. PERRIN
Department of Medical Chemistry, Australian National University, Canberra, 2600, Australia.

Analyst, 1972, **97**, 52–54.

The Determination of Nitric Oxide and Nitrogen Dioxide in Flue Gases
Part I. Sampling and Colorimetric Determination

Methods for the determination of nitric oxide and nitrogen dioxide have been evaluated for the analysis of flue gases from natural gas combustion systems: these methods have been modified where necessary. The study has included both manual and continuous instrumental methods of analysis; manual sampling and colorimetric methods are described here and continuous instrumental methods in Part II.

C. J. HALSTEAD, G. H. NATION and L. TURNER
Egham Research Laboratories, Shell Research Ltd., Egham, Surrey.

Analyst, 1972, **97**, 55–63.

The Determination of Nitric Oxide and Nitrogen Dioxide in Flue Gases
Part II. Continuous Instrumental Methods

Continuous instrumental methods based on non-dispersive infrared spectroscopy and on coulometry have been evaluated for the determination of nitric oxide and nitrogen dioxide. Instrument modifications have been made when necessary to increase sensitivity in the 0 to 100 p.p.m. concentration range. The interference caused by the presence of other components of the flue gas has been investigated.

C. J. HALSTEAD, G. H. NATION and L. TURNER
Egham Research Laboratories, Shell Research Ltd., Egham, Surrey.

Analyst, 1972, **97**, 64–69.

Potentiometric and Spectrophotometric Methods for the Determination of Bisthiosemicarbazones

A method has been developed for the quantitative determination of bisthiosemicarbazones in which addition of copper(II) chloride to a solution of the organic compound leads to complex formation. The hydrogen ions liberated on complex formation are determined by potentiometric titration. The complex, or the organic ligand itself, can also be determined spectrophotometrically.

M. J. M. CAMPBELL, R. GRZESKOWIAK, G. G. JENKINSON and I. D. M. TURNER
School of Chemistry, Thames Polytechnic, London, S.E.18.

Analyst, 1972, **97**, 70–73.

The Microbiological Assay of Total and Free Inositol with *Schizosaccharomyces pombe*

Improvements are suggested in basal medium and in methods of hydrolysis for the microbiological assay of inositol with a strain of *Schizosaccharomyces pombe*.

E. C. BARTON-WRIGHT
Galloway and Barton-Wright, Haldane Place, London, S.W.18.

Analyst, 1972, **97**, 74–76.

A New Graphite Rod for Flameless Atomic-absorption Spectroscopy

Communication

T. W. STEELE and B. D. GUERIN

National Institute for Metallurgy, Johannesburg, South Africa.

Analyst, 1972, **97**, 77.

The Determination of Lead in Biological Materials by High-energy γ-Photon Activation

Communication

J. S. HISLOP and D. R. WILLIAMS

Analytical Sciences Division, U.K.A.E.A. Research Group, Atomic Energy Research Establishment, Harwell, Didcot, Berkshire.

Analyst, 1972, **97**, 78.

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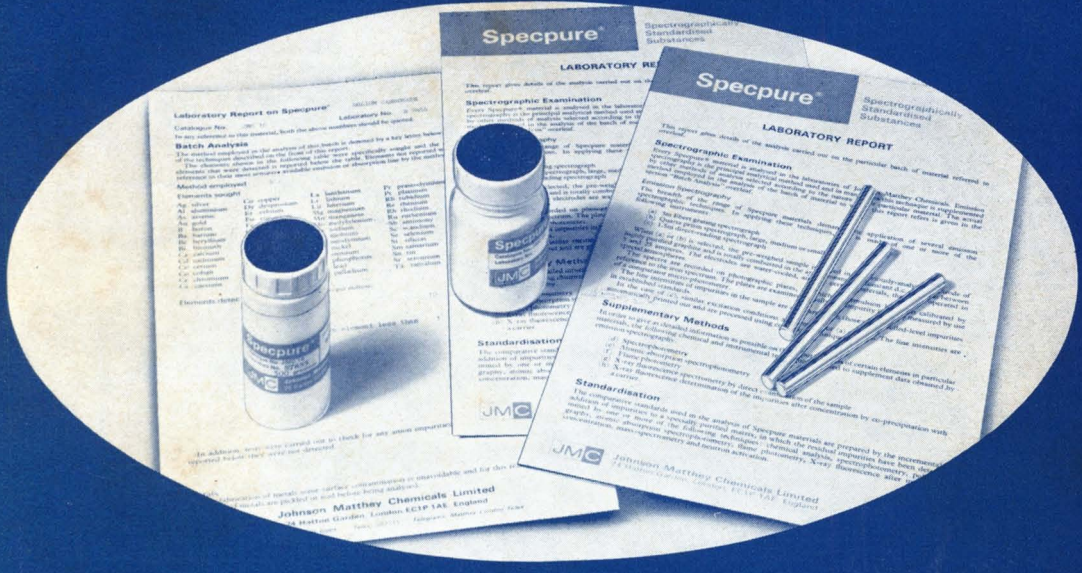

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