Trace Analysis

The following are summaries of papers presented at the Joint Meeting of the Western Section and the Microchemical Methods Group held on September 24th and 25th, 1965, and reported in the November issue of *Proceedings* (p. 164).

The Determination of Micro Constituents in Sea Water

By F. A. J. ARMSTRONG

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MR. ARMSTRONG outlined the abundance of some minor constituents of sea water and briefly discussed seasonal and geographical variations of biological importance.

Mechanical problems in sea-water analysis included the difficulties of adequate sampling and of storage. If samples were to be kept it was usual to freeze and store them at $-20°$ C. Adsorption on the walls of containers (either direct or in the bacterial film that could grow at room temperature) was troublesome. One method of solving this had been to use polythene bottles that were separately ashed and analysed. When an analysis had to be made at sea, rapid, simple and direct methods were desired; colorimetric methods were preferred.

Most chemical problems were caused by the large amount of salt present. This hindered attempts to concentrate the sample by evaporation, and could alter the sensitivity of some colorimetric methods and so cause difficulty in calibration. Magnesium could be precipitated if samples were made too alkaline. Sensitive methods were essential, dilution of the sample had to be kept to the minimum, and it was necessary to use long cuvettes in the spectro-photometers.

Analysis for nitrogen compounds had given rise to great difficulty in the past, but recent methods had used the reliable and sensitive Griess - Ilosvay method for nitrite determination, in the modern form described by M. B. Shinn. Nitrite was not normally found in appreciable concentrations in sea water, but nitrate, which was, could be reduced by amalgamated cadmium, in high yield, to nitrite. Concentrations of up to 800 μg litre^{-1} of nitrogen were found

in the deep oceans, but surface and coastal waters might have only one-tenth or less of this at most. The limit of detection was about 1 μg litre^{-1} of nitrogen. Ammonia-nitrogen, which was perhaps at one-tenth of the nitrate-nitrogen concentration, could also be converted to nitrite by oxidation with hypochlorite. The bromide in sea water acted as a catalyst, and the yield was over 70 per cent. Analysis for ammonia was still developing and some other methods were mentioned.

Phosphate was usually determined by a molybdenum blue method, the most satisfactory being a recent one involving the use of a single reagent containing acid, molybdate, a trace of antimony and ascorbic acid. The limit of detection was about 1 μg litre^{-1} of phosphorus. Local waters might contain up to 20 μg litre^{-1} of phosphorus.

Silicate was also determined by a molybdenum blue method, or less commonly as the yellow silicomolybdate. Several satisfactory methods of adequate sensitivity were in use.

Some of these methods for nutrient elements could be adapted for use in automatic analyses.

Iron and manganese could also be important biologically, and these and some of the other elements were of geochemical interest. Their analysis was complicated by the presence (at least in coastal and in surface water) of a few milligrams per litre of suspended material, which was half organic and half a mixture of silica and clay minerals. It was strongly adsorbent and could pick up trace elements from solution, and might therefore introduce a large sampling error in unfiltered samples. The absolute error might be worse still if samples were filtered and trace elements removed. Iron was mostly particulate, so that membrane filtration removed all but a few milligrams per litre. Total iron concentrations (up to about 100 μg litre^{-1} of iron) were easily determined by conventional methods with *o*-phenanthroline or bipyridine, but the results could show a coefficient of variation of ± 50 per cent. between samples. Small concentrations of iron could be measured if the sensitivity of the method was increased by using bathophenanthroline and extraction of the coloured complex. Extraction methods had also been used for copper, cadmium and lead. Co-precipitation with iron had been used for germanium, gallium, arsenic and vanadium, and co-crystallisation with thionalide for silver, and with 2-mercaptobenzimidazole for gold.

Catalytic colorimetric methods had been used for determining manganese (oxidation with periodate of tetra base or leuco-malachite green) and some work was known to be in progress on methods for determining cobalt and molybdenum. Nearly all of the sensitive techniques had been used, as for example, uranium by fluorometry, zinc by nephelometry. Direct spectrography was normally not sensitive enough, although nickel, copper, iron, vanadium, molybdenum and silver had been determined, after concentration, by extraction as the diethyldithiocarbamates. Atomic-absorption spectroscopy had given some quite promising results for copper, zinc, iron, nickel and manganese.

So far there had been little use of polarographic methods for which the sensitivity for metals had been, in the past, several orders too low. The only reported use was for the determination of nitrate in the presence of added uranyl ion. Anodic-stripping polarography was said to give useful results for cadmium and zinc. Neutron activation had been used for rubidium, antimony, barium, gold, selenium, silver, cobalt and nickel.

A brief reference was made to the analysis of organic matter, the difficulty of determining total carbon at concentrations of about 1 mg of carbon litre^{-1} by wet oxidation being mentioned. Some groups of compounds could be separated from fairly large samples and analysed by standard methods. For example, amino-acids had been determined after co-precipitation with iron or separation with 2,4-dinitrofluorobenzene. Concentrations ranged up to a few milligrams per litre. Fatty acids could be extracted with solvents and then esterified and determined by gas chromatography. In coastal waters concentrations might range up to 100 μg litre^{-1}.

There were minute, but biologically significant, amounts of vitamins such as B$_1$, B$_{12}$ and biotin, and plant hormones. Their concentrations appeared to be in the mμg litre^{-1} range and they could be determined by bioassay. Many organic compounds appeared to be concentrated in surface films.

Organic material in suspended matter was of interest in showing the nutritional properties of the crop of phytoplankton and small organisms. Material could be collected from several litres by filtration on glass filter-papers or on membrane filters, and the few milligrams obtained analysed for protein, carbohydrate, lipids, chitin and "crude" fibre by adaptations of standard methods, mostly drawn from agricultural and feeding-stuffs analysis.

The Use of the Stationary Mercury-Drop Electrode for Trace Analysis

By J. F. C. TYLER

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DR. TYLER said that most methods for determining trace elements in organic matter called for destruction of the organic matter, and that this could be achieved by a dry or wet process. The latter process was generally considered to be the more reliable and it gave, at the end of the digestion, a sulphuric acid solution containing all the minerals. Ideally, one would wish to examine this solution directly without the addition of reagents. Polarography was an attractive instrumental procedure for this, but in practice it was not satisfactory when used in the normal way with the dropping-mercury electrode. With the stationary mercury-drop electrode, however, polarography was satisfactory for it was amply sensitive and did not respond to many elements and compounds, so that interference was small.

There were many papers on this technique in the scientific literature. Much of the work had been done by Kemula. There were several excellent reviews on the subject ("Applications of the Hanging Mercury Drop Electrode in Analytical Chemistry," W. Kemula and Z. Kublik, *in* Reilley, C. N., *Editor*, Advances in Analytical Chemistry and Instrumentation, Volume 2, Interscience Publishers Inc., New York; and R. Neeb, *Angew. Chem., Internat. Edn.*, 1962, **1**, 4.) Dr. Tyler then discussed some of the results, including the peaks that could be obtained with the commercial Kemula electrode and cell coupled to a K 1000 cathode ray polarograph. The principle of the method was the accumulation of an element in, or at, the mercury drop by electrolysis, followed by anodic or cathodic stripping. Only a small proportion of the element in solution needed to be deposited in the drop. If, for example, the volume of the drop was $0 \cdot 2$ mm^3 (which was the volume of the usual 3-mg drop) and the volume of the solution was 20 ml and on electrolysis one thousandth of the total amount of the element in solution was deposited in the drop, then the concentration of the element in the drop became one hundred times that in solution. It was the response from this relatively high concentration that was measured by anodic or cathodic stripping.

Lead, cadmium and copper could be determined directly in an approximately N sulphuric acid solution. Lead had a sensitivity of $2 \cdot 5\ \mu\text{A}\ \mu\text{g}^{-1}\ \text{ml}^{-1}\ \text{minute}^{-1}$. Tin (IV) did not interfere.

Cadmium had a sensitivity of $3 \cdot 6\ \mu\text{A}\ \mu\text{g}^{-1}\ \text{ml}^{-1}\ \text{minute}^{-1}$. This was illustrated by a peak for five nanograms of cadmium in 20 ml of N sulphuric acid, but in order to obtain this, a rather long electrolysis of 25 minutes was necessary.

Copper had a high sensitivity of $6 \cdot 7\ \mu\text{A}\ \mu\text{g}^{-1}\ \text{ml}^{-1}\ \text{minute}^{-1}$, but the peaks illustrating this became distorted at low concentrations and the over-all sensitivity was about the same as other elements.

Tin(IV) could not be determined in sulphuric acid solution and it was necessary to add chloride as hydrochloric acid. The tin peak increased in height with increasing halide concentration, but at chloride concentrations greater than $2 \cdot 5$ M the rate of increase was small. This determination was subject to the same interference from lead as in the normal polarographic method, and the tin could only be determined when the tin-to-lead ratio was favourable. The response from lead in $2 \cdot 5$ M hydrochloric acid solutions was $2 \cdot 5\ \mu\text{A}\ \mu\text{g}^{-1}\ \text{ml}^{-1}\ \text{minute}^{-1}$, the same as in sulphuric acid solution; the response from tin was $3 \cdot 8\ \mu\text{A}\ \mu\text{g}^{-1}\ \text{ml}^{-1}\ \text{minute}^{-1}$.

The wave from $0 \cdot 1\ \mu\text{g}\ \text{ml}^{-1}$ of zinc in N sulphuric acid was readily observed, but because of its proximity to the hydrogen reduction wave there was no suitable base-line from which to measure its height. In $0 \cdot 01$ M acid the base-line was not entirely satisfactory, and for the precise determination of zinc it was necessary to neutralise the solution with ammonia.

Therefore, although it was not possible to determine tin and zinc directly, their determination involved the addition of only one reagent which was readily purified.

Zinc was particularly susceptible to interference due to high concentrations of other elements that were deposited with it and formed intermetallic compounds with it. Even cobalt would interfere.

Many anions could be accumulated at the mercury-drop electrode as solid films of mercurous salt. As well as halides, the anions sulphide, tungstate, molybdate, vanadate and chromate could also be accumulated and determined by cathodic stripping. (E. M. Roizenblat and Kh. Z. Brainina, *J. Analyt. Chem. U.S.S.R.*, 1964, **19**, 631.) As a practical analytical method, the determination of iodide by this technique showed promise.

The shape and behaviour of the peaks obtained on the cathodic stripping of anions were different from those obtained on anodic stripping of amalgam-forming cations. The latter peaks were of the same shape as the characteristic cathode-ray polarogram and decreased in height with successive sweeps of the cathode-ray polarograph at the rate of a few per cent. per sweep. Those of the anions were of a more symmetrical shape and they decreased in height much more rapidly.

The Sub-nanogram Region

By E. Bishop

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Mr. Bishop said that the sub-nanogram region embraced the situation in which the amount of material to be determined was of the order of 10^{-9} g or less, by virtue either of the small size of the sample available, or of the low concentration of the material in the sample. The difficulties of reagent blanks and of providing valid tests of recovery or calibrations were formidable at such levels. Not least among the difficulties encountered were those of defining what was measured and what was the meaning of the measurements made in relation to the true concentration of the test material. Both in the preparation of the calibration standards and in the handling of dilute samples it was unfortunately necessary to contain the solutions in some vessel, and even to transfer them from vessel to vessel. Even if the solution did not wet the walls of the vessel, indeed even if it were possible to isolate the sample in space, a phase boundary would exist at which adsorption or some other segregation process would occur, resulting in a change in the concentration in the bulk of the sample. The magnitude of this change was a function of many factors (*Analyst*, 1962, **87**, 845), and at concentrations of less than 10^{-5} M could amount to 15 per cent. per operation.

Despite the difficulties, however, many nuclear, chemical, kinetic and electrochemical techniques had been found to show a useful sensitivity at nanogram levels, and interest in this region had shown a rapid increase in recent times. Although the existence of such measuring techniques did not lessen the basic problems of contamination, adsorption and so on, it had encouraged investigators to give attention to them, and as the understanding of them and the methods of manipulation and measurement developed, more and more applications would be forthcoming just as had happened in the past on the microgram scale. We had already heard from Mr. Armstrong of the work in the microgram per litre range in sea-water analysis. A handful of illustrations from recent issues of one Journal would serve to emphasise the increasing activity in this region. A thin-layer cell holding 10^{-3} ml for chronopotentiometry described by Hubbard and Anson (*Analyt. Chem.*, 1964, **36**, 723) could well extend the sensitivity of the technique to 10^{-9} to 10^{-10} mole. Bombardment of iodine-containing materials with an accelerated positive gas ion beam produced secondary negative iodine ions, that could be accelerated and mass analysed. McHugh and Sheffield (*Ibid.*, 1965, **37**, 1099) had been able to detect 10^{-13} g of iodine in this way. Welford, Chiotis and Morse (*Ibid.*, 1964, **36**, 2350), using radiochromatography with ^{14}C, ^{32}P and ^{35}S labelled reagents, had detected 0·1 ng of beryllium and zirconium, and 10 ng of calcium, strontium, barium and lead. Kinetic and catalytic kinetic methods were capable of very high sensitivities. Margerum and Steinhaus (*Ibid.*, 1965, **37**, 222) had developed a method based on co-ordination chain reactions, in which EDTA and triethylenetetramine were the chain centres, and the rate of exchange with metal ions was followed by observing the colour change, which was sensitive to a change in concentration of EDTA of 10^{-9} M. Using the inhibition of fluoride ion on the action of liver esterase, McGaughey and Stowell (*Ibid.*, 1964, **36**, 2344) had estimated nanogram amounts of fluoride in the presence of phosphate by following the reaction of liver esterase on ethyl butyrate by titrating the butyric acid that had been produced with sodium hydroxide. Vanadium, in the range 0·1 to 8 p.p. 1000 m., had been determined by Fishman and Skougstad (*Ibid.*, 1964, **36**, 1643) from its catalytic effect on the rate of oxidation of gallic acid by persulphate in acid solution. Polarographic observation of the catalytic reduction wave of molybdenum(VI) in the presence of nitrate had been shown by Violanda and Cooke (*Ibid.*, 1964, **36**, 2287) to yield a sensitivity of 5×10^{-9} g ml^{-1} of molybdenum. The rapidly rotating gold electrode had been shown by Miller, Long, George and Sikes (*Ibid.*, 1964, **36**, 980) to respond linearly to cyanide ion in the ranges 10^{-6} to 10^{-10} and 10^{-11} to 10^{-15} g. Activation analysis and anodic-stripping voltammetry had long been established in this region.

Among the electrochemical methods for trace analysis, the combination of differential electrolytic potentiometry with amperostatic coulometry had proved fruitful as well as cheap and simple.   With silver indicating electrodes and a medium 10^{-2} M in nitric acid and 80 to 90 per cent. methanol, 10^{-11} mole of chloride or bromide in a volume of 0·5 to 1·0 ml had been determined with an accuracy of 2 to 15 per cent., depending on how effectively adsorption losses could be corrected.

Mr. Bishop then described the apparatus and method, and discussed the results which he and Dhaneshwar (*Analyt. Chem.*, 1964, **36**, 726) had obtained.

Judging by the requests for advice on particular problems, the demand for determining chloride at low levels was extensive, but as yet the full sensitivity of the method had not been required, 10^{-10} mole being the smallest amount so far notified.   The authors remained sceptical of the validity of the results, but despite an extensive search had been unable to locate any source of spurious signals.   Independent confirmation down to 10^{-10} mole had been reported, but full confirmation was awaited before the results could be considered completely acceptable.   So far, reported failures of the method had been traced to three causes: failure to activate the electrodes properly, use of de-ionised water at some stage in the proceedings or use of synthetic detergents for cleaning equipment, the latter two factors leading to de-activation of the electrodes.

In the halide determinations, no visible precipitate was produced.   The product of the concentrations of chloride and silver ions at the lowest determination level could not exceed 10^{-16} mole^2 litre^{-2}, yet the conventional solubility product of silver chloride is of the order of 10^{-10} mole^2 litre^{-2}, and, although the solvent is partly methanol, it still contains some 20 per cent. of water, and the depression of solubility product by the organic solvent could not account for the production of analytical signals at concentration levels some 10^{-6} times the failure level of conventional methods and 10^{-3} times the molar solubility of silver chloride. New ideas on solution chemistry and electrode reactions were clearly needed if these phenomena were to be explained.   As yet Mr. Bishop said, experimental evidence was lacking, and so it could only be tentatively suggested that the solution reaction was ion-pair formation and that adsorption overpotentials contributed to the electrical signals.

The Determination of Trace Contaminants in Peroxygen Compounds

By C. Whalley and D. B. Adams

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Mr. Adams said that the problems involved in the analysis of hydrogen peroxide were rather different from those for other inorganic peroxygen compounds and he would therefore treat them separately.   Hydrogen peroxide was manufactured at the present time by an auto-oxidation organic procedure.   This involved the cyclic reduction and oxidation of 2-ethyl anthraquinone in a mixed organic solvent.   The hydrogen peroxide formed was extracted into water and purified by distillation.   This process gave a high purity product—the impurity content being similar to that of good quality de-ionised water.   There were a number of special contaminants.   Most of these were carbon compounds of various kinds arising from the organic process.   Phosphate or tin or both were added to certain grades as stabilising agents, and aluminium was often present due to the storage of the material in aluminium tanks.   The approximate order of concentration of these impurities was indicated in Table 1.   It was emphasized that the hydrogen peroxide sold as an analytical-grade reagent contained no tin, although it did contain a slight trace of phosphate.

TABLE I

IMPURITIES IN HYDROGEN PEROXIDE

Contaminant				Amount, mg litre^{-1}
Carbon (as C)	..	..	..	2 to 200
Phosphate (as PO$_4$)		..	..	0·1 to 250
Tin (as Sn)	..	..	..	0 to 10
Aluminium (as Al)	..	..	..	0·02 to 2

The most important determination carried out on hydrogen peroxide was that of stability.

The material was extremely sensitive to trace-metal contamination and great care had to be taken to obtain reliable results. A good sample of 85 per cent. w/w hydrogen peroxide might lose 0·1 ml of oxygen per minute per 25 ml of sample at 100° C. An addition of 1 μg of copper per 25 ml, *i.e.*, 0·04 mg litre^{-1} of copper, increased this rate 7 times.

There were a number of important ways of accomplishing the decomposition of the sample before analysis, such as addition of catalytic ions, *e.g.*, iron, copper, cobalt, the provision of catalytic surfaces, *e.g.*, precious metals or the hydroxides and oxides of heavy metals, and increasing pH. Often a combination of these was used to achieve rapid and complete decomposition.

Phosphate was determined by a standard molybdenum blue method with ascorbic acid as the reductant. For the higher levels of phosphate, the vanado phospho-molybdate procedure was used. The phosphate was sometimes present as pyrophosphate and had to be hydrolysed before completion of the determination. The organic matter present could interfere with low-level phosphate determinations and should therefore be destroyed. Aluminium had been determined by the aluminon method, but the 8-hydroxyquinoline method was more suitable under these conditions, as possible interfering metals were present in low concentration. The interference of iron could be suppressed if necessary by adding *o*-phenanthroline before the extraction procedure. Again pyrophosphate and carbon compounds could interfere with the analysis. A polarographic method had been used for determining low concentrations of tin. After decomposition the sample was fumed with sulphuric acid to ensure that all the tin present was in true solution, as tin could be colloidal in the hydrogen peroxide. The final solution was polarographed in ammonium chloride base electrolyte. The total carbon content was determined by decomposing a small sample with a manganese dioxide slurry and igniting it in a stream of oxygen. The carbon dioxide evolved could be sometimes determined by a classical titrimetric method, although the conductometric finish after absorbing in baryta had been satisfactory. The carbon dioxide formed could also be determined by gas - liquid chromatography.

With inorganic peroxy-compounds such as sodium perborate, stability was again a considerable problem. The particular impurities in this compound were copper, cobalt, manganese and, surprisingly, mercury, arising from the raw materials. Iron was usually present in relatively large amounts and had to be allowed for in any scheme of analysis. The approximate levels found were iron, 5 to 10 p.p.m., copper and manganese, 0·1 to 1 p.p.m., cobalt, 0·01 to 0·1 p.p.m. and mercury occasionally up to 0·1 p.p.m.

Stability was determined by measuring the decrease in activity after storing for 9 days at 55° C. The catalytic action of ions such as cobalt, on the oxidation of alizarin by sodium perborate had been used as a method of detection. Unfortunately, this was not a selective reaction and could not be used for individual determinations.

Mercury had been determined when necessary by the Růžička - Starý substoicheiometric radiometric method, with a limit of detection of about 0·1 p.p.m. This had been moderately successful although this determination was only required in exceptional circumstances. To obtain sufficient sensitivity in the determination of other metals it had been necessary to use a concentration procedure before the actual determination.

It was essential in trace-metal analysis to ensure that the metals being determined were in true solution at the start of the analysis. This was difficult with an inorganic compound such as sodium perborate where the chemical state of the metals was not known. Fairly drastic methods might be necessary if the metals were present as refractory oxides. From the stability point of view, these were just as important as metal ions. It was suggested that insufficient attention was normally paid to these points.

The method finally used was to extract the metals, as the diethyldithiocarbamate complexes, into chloroform at pH 8·5. The chloroform extract was evaporated to dryness and the metals obtained in a small volume of hydrochloric acid solution. A scheme of successive solvent extraction and colorimetric measurement was devised that would cope with six metals, *i.e.*, vanadium, copper, iron, cobalt, manganese and chromium. Vanadium and chromium were included although they were not extracted as diethyldithiocarbamate complexes under the conditions used. Vanadium was extracted into chloroform, as its phenyl benzohydroxamic acid complex, from 6 N hydrochloric acid. Copper was extracted from the same solution as its dibenzyldithiocarbamate derivative. In both of these the extract could be used directly for colorimetric measurement. The solution was then diluted and iron extracted as the cupferrate. The cupferron extract was wet oxidised and a standard

o-phenanthroline procedure was used to determine iron.   The main solution was then adjusted to a pH of between 4 and 6, and cobalt extracted as the 2-nitroso-1-naphthol complex.   Manganese was extracted with diethyldithiocarbamate and finally determined as permanganate. The remaining chromium was oxidised to chromate and determined by a standard diphenyl carbazide procedure.

All the methods mentioned were suitable for the determination of between 0·1 and 1 μg of the respective elements.   About 40 g of original sample was taken for the diethyldithiocarbamate general extraction so that the level of sensitivity required was easily obtained.

The Determination of Some Impurities in Beryllium by Differential
Cathode-Ray Polarography

By G. C. GOODE AND J. HERRINGTON

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MR. GOODE said that the presence of impurities in beryllium could have profound effects on its nuclear and physical properties, and extensive trace analysis was often necessary.

Differential cathode-ray polarography with the subtractive technique was particularly useful at very low concentrations as subtraction of unwanted currents from reagents and supporting electrolyte enabled the maximum instrumental sensitivity to be utilised.

This technique had been applied to the analysis of the high purity beryllium used as a reference material in metallurgical research and for which relatively small samples were available.

Methods were described for the determination of copper, lead, cadmium, zinc, nickel, cobalt, manganese and iron to a limit of 0·5 p.p.m. on a single 500-mg sample and for chromium and uranium to 1 p.p.m. on separate 200-mg samples.

Elements other than uranium are separated by solvent extraction of diethyldithiocarbamates into ethyl acetate from beryllium chloride or nitrate solutions at pH 4·5.

The high solubility of the reagent in water and of the complexes in the solvent enabled small volumes to be used and this, in conjunction with semi-micro techniques, reduced reagent blanks to a minimum.   The lack of specificity of the extraction, however, necessitated careful selection of supporting electrolytes to avoid interferences.

Organic matter was destroyed before polarography by dry ignition in a silica vessel at below 500° C in the presence of a small amount of potassium chloride, without apparent loss of trace element.

Orthophosphoric acid of molar concentration was used for the determination of copper, lead and cadmium; the close proximity of zinc and hydrogen-ion waves, however, prevented quantitative determination of zinc at low concentrations.   Interference from the irreversible reduction of molybdenum(VI) on lead was eliminated by measurement on the reverse sweep.

Manganese was determined in M potassium chloride, iron(III), a serious interference, being previously extracted into ether from a 6 M hydrochloric acid solution and subsequently determined in 0·1M ammonium oxalate.

Addition of a few drops of pyridine to the potassium chloride electrolyte enabled nickel, cobalt and zinc to be determined.   Although resolution of zinc and cobalt was impossible on the forward sweep in this electrolyte, a single zinc peak was obtained on the reverse sweep due to the irreversibility of the cobalt reduction.   For up to a 10-fold excess of zinc it had been shown that cobalt could be quantitatively determined on the forward sweep if the zinc wave was eliminated by addition of a zinc standard to the reference cell.

Chromium was also extracted from beryllium as the diethyldithiocarbamate complex, but oxidation to chromium(VI) was necessary before extraction.   For this, oxidation with bromate ions, in the presence of nitric acid, was satisfactory and chromium(VI) was finally determined in M mannitol - 2M sodium hydroxide supporting electrolyte.   Uranium(VI) was extracted from a nitric acid solution of beryllium into ether at a total nitrate concentration of greater than 6M, and 2M sulphuric acid was used as the supporting electrolyte.   Reproducible reagent blanks, not greater than 0·3 μg, were obtained for each element and recoveries were quantitative at the 0·5-μg level in the presence of beryllium.

Replication of polarographic results for samples of high purity electrolytic flake was satisfactory and in good agreement with those obtained by emission spectroscopy.

The Application of Some Ternary Systems in Trace Analysis

By R. M. Dagnall

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Dr. Dagnall said that ternary systems produced by the reaction between certain transition-metal ions, nitrogenous bases and anionic dyestuffs could be used for the photometric or fluorimetric determination of trace amounts of these metal ions. The particular advantages of such systems were their selectivity, obtained by suitable choice of the nitrogenous base, and high sensitivity (molecular extinction coefficients of the order 80,000 to 90,000). In addition they could be used in aqueous or organic media over a pH range at which masking agents could be used if necessary.

The development of these systems arose from the observation that the reagent system 1,10-phenanthroline - bromopyrogallol red ($\lambda_{max.} = 560$ mμ) produced, with silver ions in aqueous solution, an instantaneous blue-coloured solution ($\lambda_{max.} = 635$ mμ) of very high intensity ($\epsilon_{max.} = 51,000$). The colour reaction could be obtained over the pH range 3 to 10, although the optimum pH appeared to be about 7. This blue-coloured ternary system, which was found from photometric studies to be an ion-association system [(phen-Ag-phen)$^+$]$_2$BPR^{2-}, was stable and was the basis of a method for the determination of trace amounts of silver. The procedure, which involved extraction into nitrobenzene and the use of mercuric ions and EDTA as masking agents, was free from the interference of the 27 cations and 15 anions investigated. Only large amounts of gold and thiosulphate were found to interfere.

A new aspect of the method was the elimination of interference from anions that normally reacted with silver ions in aqueous solution, e.g., iodide, cyanide, and thiocyanate. A double-masking action was used whereby a sufficient excess of mercury(II) ions was added to the solution to complex these anions. Excess EDTA was then added to complex the excess mercury(II) ions.

The use of nitrobenzene, which was found to be the only solvent capable of extracting the complex, overcame the problems of precipitation of the complex in aqueous solution with large amounts of silver and the interference of a large excess (about 1000-fold mole excess over silver) of certain anions, but resulted in a reduction in sensitivity ($\epsilon_{max.} = 32,000$). This however, was still superior to the standard dithizone and p-dimethylaminobenzalrhodanine methods.

Bromophenol blue had been recently found to be superior to bromopyrogallol red as the anionic component in view of its greater stability to oxidation and the lack of unnecessary o,o'-dihydroxy-complexing centres. In addition, the use of the divalent-silver complex, prepared by the addition of ammonium persulphate to silver(I) ions, gave a substantial increase in sensitivity because of the now more favourable metal-to-dyestuff ratio.

It had been thought that the use of nitrobenzene, due to its rather unpleasant nature, introduced new practical difficulties. Consequently, similar systems had been investigated with a view to the use of other solvents. Particular attention had been directed to the reactivity of other metal ions and dyestuffs (especially those containing carboxylic acid groupings) with 1,10-phenanthroline and its near relatives.

In general, the ternary systems of the greatest potential analytical utility were those formed by the association of the positively charged 1,10-phenanthroline complexes of zinc, cobalt(II), nickel, cadmium, manganese, lead and copper(II) with the negatively charged fluorescein class of dyestuffs, e.g., tetra-iodo(R)fluorescein (erythrosin). Each of these complexes could be extracted into solvents such as chloroform and ethyl acetate and some of them, e.g., copper(I), cadmium, manganese and zinc, yielded a direct positive fluorescence in the organic phase. The remaining complexes, after dilution of the organic phase with ammoniacal acetone, also gave a positive fluorescence. The fluorescence corresponded to that of the free dyestuff. However, the colour change observed in aqueous solution tended to suggest that these ternary systems could not be considered to be merely a simple association of oppositely charged species.

Although the silver - 1,10-phenanthroline - erythrosin complex was only soluble in nitrobenzene, the corresponding pyridine complex was quite soluble in both chloroform and ethyl acetate. This also gave a positive fluorescence directly after extraction. Fluorescent

methods of analysis, based on the above complexes, were of particular interest because there was a dearth of methods yielding a positive fluorescence for those transition metals that contain partially filled d-electron levels.

Copper(II) was selected as a model metal ion for investigating both photometric and fluorimetric methods of analysis, based upon reaction with 1,10-phenanthroline and erythrosin, coupled with extraction into chloroform.

The basis of the spectrophotometric determination involved the standard extraction of the cuprous-2,9-dimethyl-1,10-phenanthroline complex into chloroform at pH 6 (citrate buffer) in the presence of EDTA to achieve a specific extraction of copper. The organic phase was then separated and equilibrated with an aqueous phase containing 1,10-phenanthroline and erythrosin at pH 9 (phosphate buffer). The coloured organic extract was finally measured at 545 mμ in a 1-cm cuvette.

The addition of 1,10-phenanthroline, before the second extraction converted copper(I) to copper(II) and so gave a more favourable metal-to-dyestuff ratio. The molecular extinction coefficient at the maximum wavelength of absorption is 62,000.

The spectrofluorimetric determination involved basically the same procedure but with the addition of ammoniacal acetone to the final organic phase. The fluorescence was measured at 555 mμ with excitation at 340 or 535 mμ. The advantage of this method was that it increased the sensitivity at least 10-fold compared with that of the spectrophotometric method.

By the use of these methods, and without the extraction system as a means of concentration, the determination of copper in the range 0·6 to 6·0 p.p.m. (spectrophotometric) and 0·06 to 0·6 p.p.m. (spectrofluorimetric) could be made.