

SOME RECENT DEVELOPMENTS IN METHODS OF SEPARATION

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ABSTRACT

Separation methods are being applied more extensively than ever before, particularly in trace analysis. Some of the more interesting procedures which have recently been proposed in solvent extraction and ion-exchange chromatography are reviewed, together with other new procedures for separation based on classical techniques. The possibilities of gas chromatographic separation of metal chelates are briefly discussed.

Despite notable advances in the development of selective reagents, masking agents and selective instrumental methods, the literature on methods of separation is still expanding rapidly. This is partly because the special circumstances which demand prior separations are multiplying, and partly because more efficient separation methods have become available and are being applied widely.

Solvent extraction seems to be the preferred approach and some notable advances have been made during the last few years; however, other methods have not been neglected and many possess interesting features. This account is influenced by the interests of the author, but the selected methods which are presented probably give a fair idea of recent progress. Particularly noteworthy is the fact that efficiency of separation is so often checked nowadays by radiochemical methods.

SOLVENT EXTRACTION

A new departure in liquid-liquid extraction has been described: liquid-liquid extraction is followed by solid-liquid extraction. The determination of copper as its 8-hydroxyquinoline complex serves to illustrate the technique¹. Reagent pellets are prepared by melting together 8-hydroxyquinoline and diphenyl. The solid pellet is dropped into the test solution, which is heated to above the melting-point of the pellet (90°C), and then the container is well shaken. It is allowed to cool and the solidified pellet now contains the copper complex. After removal of the aqueous layer, the pellet is dissolved in chloroform and the absorbance is measured. This procedure overcomes difficulties associated with slow attainment of the distribution equilibrium and with poor separation of phases.

Other metals which have been determined by such processes are zinc and magnesium (as oxinates with naphthalene as solvent)².

For multiple extraction, dithizone is undoubtedly one of the best solvents. Unfortunately, the chlorinated solvents which are used in conjunction with dithizone, prohibit final measurement by atomic absorption spectroscopy. After an examination of various solvents, Sachdev and West³ concluded that ethyl propionate was the best; it burns smoothly in an air-acetylene flame and the metal dithizonates remain stable. The following ions were extracted: Ag^+ , Cd^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} . It would seem that very few other metals interfere and this procedure provides a rapid and convenient separation for use with measurement by atomic absorption spectroscopy.

A simple method for the separation of rhenium from Mo, W, Cr, V, Se, Te, and Os is based on extraction with acetylacetone from alkaline solution (0.5M sodium hydroxide)⁴. The procedure has some advantages, for most of the metals which interfere with the determination of rhenium separate as hydroxides. The method seems useful for the removal of major amounts of molybdenum, but it is necessary to remove the final traces by extraction as the oxinate. This minor disadvantage also exists in the alternative method of the same authors based on extraction with isoamyl alcohol from peroxide-1M phosphoric acid medium⁵.

2-Ethyl-1-butanol, 4-methyl-2-propanol and 1-butyroxy-2-propanol extract a number of metals selectively from iodide-containing sulphuric acid solutions⁶. Some interesting separations are possible, e.g. zinc and cadmium with 2-ethyl-1-butanol or 4-methyl-2-pentanol, and indium and gallium with either of these alcohols or 1-butoxy-2-propanol.

There are very few methods available for the determination of cobalt in its different oxidation states. Polarography, potentiometry and spectrophotometry have been used, but the methods appear to be unsatisfactory. In a new approach, solvent extraction is used and provides a clean separation of cobalt(II) and cobalt(III) so that any suitable finish may be applied⁷. The sample is reacted with hot acetylacetone and diluted with 20 per cent acetic acid. The cobalt(III) complex is extracted with benzene, the solution is diluted with *n*-pentanol, and cobalt is determined by atomic absorption spectroscopy. The separated cobalt(II) in 20 per cent acetic acid can be determined likewise; spectrophotometric and EDTA titration provide alternative finishes. Even at low concentrations (0.01 per cent) accurate results can be obtained.

Several solvents have been recommended for the separation of heteropolyacids, and methods have been based on such separations for the determination of phosphorus, arsenic, silicon and germanium. In all these methods, titration, spectrophotometry or atomic absorption spectroscopy are used to complete the determination. A method for the determination of phosphorus in the presence of arsenic was required⁸ and as gravimetric methods were considered preferable for accurate work, a range of solvents was re-examined using phosphorus-32 and arsenic-74. It was confirmed from the count-rates that *n*-butyl acetate was the most suitable extractant and gave the best separation from arsenic. Heptanol extracted rather more arsenic, and iso-octanol was unsatisfactory for gravimetric work as the layers were difficult to separate. Phosphorus was determined in steels containing arsenic by weighing ammonium phosphomolybdate, precipitated after extraction and back-extraction; excellent separations were obtained.

Free hydrocyanic acid, rather than the cyanide ion, in rivers is responsible

for high mortality amongst fish; hence it is necessary to differentiate this substance from cyanide ion. It is important to avoid disturbing the equilibrium during analysis and it is, therefore, essential to separate hydrocyanic acid from the system. It has been found that 1,1,1-trichlorethane extracts hydrocyanic acid and the equilibrium system is not significantly disturbed⁹. It is necessary to determine the cyanide spectrophotometrically in aqueous solution; for this purpose sodium pyrophosphate was found best for the back-extraction.

The separation of boric acid from complex systems has always been a major problem. The only reliable method, which has been in use since 1887, consists of distillation as the methyl ester. This method is tedious and a convenient simple extraction method has long been sought.

Agazzi¹⁰ recommended 2-ethylhexanediol-1,3 (EHD) as a selective solvent, for it was known to form complexes with boric acid. He used atomic absorption spectroscopy to determine the boron in the extract. Traces of certain other metals [vanadium(v), iron(III)] were also extracted but did not interfere. The method was examined in our Department¹¹ and was found to work well with pure solutions. However, the other metals which were extracted in traces interfered with the particular spectrophotometric method used to measure boron. Prior extraction with cupferron and other methods of separation were troublesome and cumbersome, but it was concluded that within certain limits, the method had possibilities.

More recently, a more fundamental study of EHD and another 1,3-diol (2,2-diethylpropane-1,3-diol) has been made¹². This showed that a 1 : 2 boric acid-diol complex is formed in the chloroform phase in two steps and that the equilibrium constant for the first step is considerably larger than that for the second. Above pH 8 there is a decrease in the distribution ratio owing to the formation of $B(OH)_4^-$. It is considered that the diols are monomeric in the aqueous layer, but in the chloroform layer there is a dimer and polymer besides the monomer. The need for more effective diols is discussed.

More recently 3-methylbutane-1,3-diol has been recommended¹³ and appears to be more successful. A wide range of cations and anions including iron(III) and copper(II) did not interfere. The determination was completed titrimetrically and gave an error of below one per cent.

ION EXCHANGE

Insoluble salts of heteropolyacids have been used for some years as cation exchangers. Generally, ammonium molybdophosphate (AMP) is used. A refined method for separating sodium and potassium from each other and from other ions has been developed using AMP columns¹⁴. As little as 0.1 meq of potassium can be separated from amounts of sodium up to 50 meq. Dilute nitric acid and ammonium nitrate solutions, respectively, are used to elute sodium and potassium. After separation, the solutions are passed through a strongly basic anion-exchange column and the hydroxides are titrated with 0.01M hydrochloric acid. Other cations are separated by preliminary separations on a conventional ion-exchange column. It is not certain how other alkali metal ions behave, but it seems probable from the K_D values quoted, that lithium would be eluted along with sodium, whereas rubidium and caesium would remain

adsorbed after elution of potassium. However, the method appears to give a rapid and clean separation of the two commoner alkali metals.

Cellulose phosphate has been recommended for the same purpose¹⁵. Sodium-24 and potassium-42 are separated by ion-exchange chromatography with 80 per cent methanol-2M hydrochloric acid as the eluent. Sodium is eluted in the first 30 ml and potassium in the 50-80 ml fraction. The absolute amounts separated were 10^{-2} - 10^{-3} mole of each element. Paper chromatographic separation on strips of the same material was also possible.

The accurate determination of calcium and magnesium is hindered by the difficulty of separating them efficiently from iron, aluminium, titanium and manganese. Precipitation methods, masking, separating by solvent extraction each provide their own handicaps. The titration of calcium and magnesium in the presence of each other also provides difficulties.

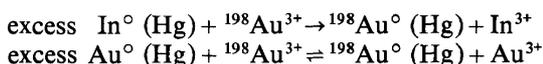
A simple ion-exchange method has been developed¹⁶ which separates calcium and magnesium from many other metals and from each other. All interfering elements are eluted from a column of Zeo-Carb 225 cation exchanger (ammonium form) by ammonium-EDTA at pH 4.5. Calcium and magnesium remain on the column, and can be washed out successively with a solution of ammonium chloride. Barium and strontium still remain and presumably could be eluted with stronger ammonium chloride and determined by flame photometry. The separated magnesium and calcium are titrated with EDTA, preferably using a photoelectric titrator.

Magnesium, calcium and strontium can be separated on a column of zirconium molybdate¹⁷. The components are eluted successively with methanolic ammonium sulphate solution, ammonium nitrate-nitric acid, and ammonium nitrate solution, directly into buffer solution and are then titrated with EDTA. Efficient separations are achieved.

OTHER METHODS

The separation of tin and indium is a problem associated with the control of indium concentrates. Several precipitation methods have been proposed, but detailed studies of their efficiency are lacking. A simple and efficient method has been developed¹⁸ based on precipitation of tin from weakly ammoniacal solutions in the presence of EDTA. The efficiency of separation was checked by the use of radioactive tin and indium. Indium remains almost completely in solution, together with one to two per cent of tin. It is necessary to maintain the concentration of EDTA within an optimal range. At high concentrations the precipitation of tin is impeded, whereas at low concentrations, the separation of indium is incomplete.

A rapid procedure for the separation of radioactive gold from a wide variety of materials has been recommended¹⁹. Both isotopic exchange and chemical reduction of $^{198}\text{Au(III)}$ in acid solution, by a dilute liquid indium-gold amalgam takes place as follows:



The counting efficiency for ^{198}Au in small volumes of the amalgam is high.

There are few interferences and the method can be applied to clays, rocks, salts and metals. The method could probably be used for the separation of other noble metals.

As methods for the separation of manganese from complex mixtures (precipitation, solvent extraction or ion-exchange) are time-consuming, the little-used method of distilling permanganic acid has been examined²⁰. A method was required for use in trace analysis after neutron activation and for the preparation of carrier-free manganese-54 from iron cyclotron targets. The solutions were heated with concentrated sulphuric acid and periodate. Recoveries between 60 and 90 per cent were obtained, the losses being due to deposition of manganese dioxide. Yields were improved by passing hydrogen chloride through the condenser to solubilize the manganese dioxide; iron and cobalt were not carried over by this treatment as shown by tracer experiments. Chromium had no significant effect. The overall yield was 85 to 90 per cent.

Silicate is generally supposed to interfere with the precipitation of phosphate as ammonium phosphomolybdate, although the mechanism is never clearly stated in textbooks. Some authors imply that gelatinous hydrated silica slows down filtration, whereas others state that ammonium silicomolybdate is co-precipitated. Certainly bases such as quinoline or 8-hydroxyquinoline precipitate both heteropoly anions quantitatively.

Feigl²¹ describes a test for silica in the presence of phosphorus which suggests that ammonium silicomolybdate does not interfere with the precipitation of ammonium phosphomolybdate; investigations based on this observation led to the development of an efficient method for the separation of the two elements within certain concentration ranges²². Phosphate is precipitated as ammonium phosphomolybdate and all the silicate (as silicomolybdate) passes into the filtrate. It is precipitated as quinoline silicomolybdate and determined gravimetrically or titrimetrically. The ammonium phosphomolybdate is dissolved in dilute ammonia solution and the phosphate is precipitated as quinoline phosphomolybdate which is determined similarly.

A simple method for the separation of large amounts of sodium has been described²³. Hydrochloric acid gas (or hydrochloric acid) is added to the solution and sodium is precipitated. The procedure is especially useful after a fusion with sodium salts and enables small chromatographic columns to be used in any further operations. When the solution is 12M in hydrochloric acid, only about 0.75 mg of sodium chloride per millilitre remains undissolved: at 10N about 1mg/ml remains. The efficiency was checked by estimating ²⁴Na in the supernatant solution. Better than 96 per cent recoveries of ⁸⁹Sr, ¹³⁴Cs, ⁶⁰Co, ⁵¹Cr(III), ⁴⁶Sc, ¹⁵³Gd, ¹²⁴Sb, ²³³Pa were achieved. Double precipitation gave quantitative recoveries of all these elements.

The first general account of a possible new method of separation in inorganic analysis was described by Moshier and Sievers²⁴. In this method metals as their volatile chelates are separated by gas-liquid chromatography. Many interesting separations appear to be possible, but the technique still requires considerable study before it can be applied with confidence as an analytical tool. There is room for the development of new ligands and, to overcome some of the undesirable adsorption effects, new stationary phases.

Separations on the preparative scale (100 mg of sample) of iron, chromium and aluminium as their trifluoroacetyl-pivaloyl-methanes have been achieved.

Each metal chelate can be separated from mixtures containing two per cent of the other metal chelates on a 20ft column. The separation of the chromium chelate is particularly effective; chemical analysis of the eluted materials showed that the amount of residual chromium was 0.09 per cent in the aluminium chelate and 0.027 per cent in the iron chelate. Several other metal chelates have been successfully separated on this scale, but so far no advantageous *analytical* methods have been forthcoming²⁵.

Separation of the same chelates by zone-melting has been examined, but preliminary experiments indicate that this process is inferior to the GLC method²⁶ as a means of preparing pure substances.

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