

S 63. *A New Method for the Detection and Determination of Uranium.*

By T. V. ARDEN, F. H. BURSTALL, and R. P. LINSTEAD.

A chromatographic method employing organic solvents in conjunction with strips or sheets of absorbent paper is described for the separation of uranium from other metals in solution. Uranium as uranyl nitrate is dissolved and moves with the solvent front as diffusion of the solvent in the absorbent paper proceeds. Most other metals remain stationary or move only slowly in comparison with uranium. Detection is accomplished with potassium ferrocyanide while quantitative determination is achieved by removal of the portion of paper containing the uranium, followed by measurement with the polarograph, colorimeter, or fluorimeter.

THIS paper describes a new method for the detection and determination of uranium in a very wide variety of materials. The essential feature of this method is the use in combination of an organic solvent and a solid adsorbent such as cellulose. This technique employing organic solvents and solid adsorbents for the separation of chemical entities was first used by Gordon, Martin, and Synge (*Biochem. J.*, 1943, **37**, 79) for the separation of mixture of amino-acids, and it has since been applied to a number of other organic separations. The application of this process to inorganic chemistry was first studied at the Chemical Research Laboratory at the end of 1946 and a preliminary account of these investigations as applied to materials other than radioactive elements has been published (Arden, Burstall, Davies, Linstead, and Lewis, *Nature*, 1948, **162**, 691; Burstall, Davies, Linstead, and Wells, *ibid.*, 1949, **163**, 64; Linstead, Discussion on New Techniques, Chemical Society, November 25, 1948). Other workers have also reported similar separations of inorganic substances (Lederer, *Nature*, 1948, **162**, 776; Pollard, McOmie, and Elbeth, *ibid.*, 1949, **163**, 292).

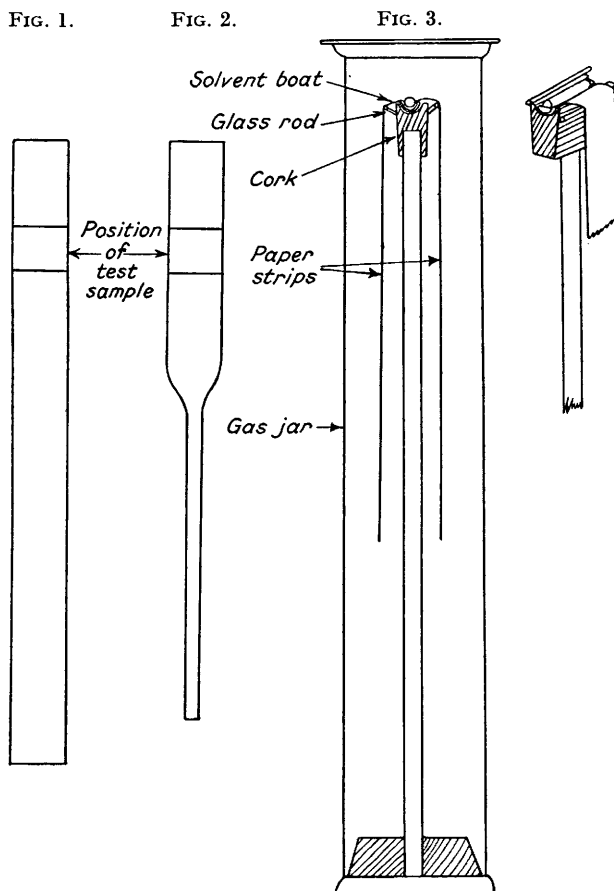
Uranium was among the first elements which we examined in 1946, since the high solubility of uranyl nitrate in organic solvents was considered to favour a separation from other elements. This view has been fully justified by the development of a precise and rapid procedure for the detection and determination of uranium.

This method depends on the selective extraction of uranyl nitrate by an organic solvent containing nitric acid and is carried out on a strip or sheet of absorbent paper. The organic solvent mixture is allowed to diffuse by capillary action through the paper, and when this solvent movement takes place over a patch of the paper previously treated with a sample of the solution to be tested, uranyl nitrate is dissolved and moves with the solvent front as diffusion proceeds. In general, uranium is separated from other elements which either remain stationary or move only slightly in comparison with it. For qualitative and semi-quantitative work, the uranium is made visible by treatment of the paper with aqueous potassium ferrocyanide. This gives the characteristic brown stain of uranyl ferrocyanide which, under favourable conditions, appears as a sharp and uniform band near the limit of solvent movement. This technique is sufficiently sensitive to yield a positive result with as little as 0.1 μg . of uranium, and a rough quantitative estimation with an accuracy of about $\pm 30\%$ is possible with 0.25 μg . and up to 200 μg . by visual comparison with standard stains produced with known quantities

of uranyl nitrate. This paper-strip technique is not restricted to qualitative or semi-quantitative estimations but has been developed by Mr. J. A. Lewis, of this Laboratory, to a full quantitative process by removing the section of paper containing the uranium, ashing the paper to remove organic matter, dissolving the residual uranium in acid, and determining it by means of the polarograph. Colorimetric and fluorimetric methods have also been used with success in final determinations of uranium. All these quantitative methods will be described in future communications.

EXPERIMENTAL.

Apparatus.—Filter-paper (Whatman No. 1) is cut into strips of 8–12" long and 1" wide and the sample of solution to be tested is placed at 3–4" from one end of the strip so that a small patch about 1" square is formed (Fig. 1). If very small quantities of uranium are involved, the filter-paper strip is cut in a roughly spade shape or triangular form to provide for a larger quantity of test liquid and to give a narrow portion to enhance the uranium band on development with potassium ferrocyanide (Fig. 2). The remaining equipment consists of a cylindrical gas jar or similar vessel fitted with a small container for the organic solvent near the top, as shown in Fig. 3. The end of the paper strip nearest the test patch is made to dip into the solvent tank, while the other end hangs vertically in the jar.



Preparation of Samples.—In the absence of phosphate, solutions in 25% nitric acid are used without further chemical treatment. The most appropriate method for obtaining such solutions depends on the type of product under investigation. With the minerals and ores principally studied by this method, decomposition with (a) nitric acid with addition of hydrofluoric acid and perchloric acid, (b) potassium hydroxide or sodium peroxide fusion with subsequent treatment with nitric acid, have proved most useful. Sulphuric acid and bisulphates are avoided for breakdown of mineral products since a high proportion of sulphate ion is undesirable in this extraction method. It is necessary to complex phosphoric acid by ferric nitrate with products containing a large amount of this acid, but small quantities do not interfere with the extraction. The solutions prepared as indicated are made up

by volume and a small measured portion (0.05 ml.) placed on the paper strip and air-dried. For larger quantities, up to 0.15 ml. of test solution, a thicker paper (Whatman No. 3) or several successive additions with air-drying after each addition are required.

Solvents.—A very wide range of organic solvents which dissolve uranyl nitrate can be used in this process. These solvents contain oxygen and include ethers, alcohols, ketones, esters, and acids. The best results so far achieved have been obtained by using the cyclic ethers 2-methyltetrahydrofuran and tetrahydropyran. Nitric acid (*d* 1.42) is added in quantities of 2.5 and 10% by volume respectively to these solvents, and the mixture just saturated with water. The process is not, however, dependent on the use of these special solvents and others such as methyl *n*-propyl ketone, methyl *isobutyl* ketone, cyclohexanone, Cellosolve acetate, *n*-butyl alcohol, ethyl acetate, etc., enable the uranium to be separated. Substantial variations are shown in the time required for the solvent to diffuse through the paper strip, and in the sharpness and position of the uranium band relative to the solvent front, as well as in the effectiveness of separation from other metals. It is also significant that solvents completely miscible with water such as acetic acid and acetone have been used although with less satisfactory results for uranium. The quantity of solvent mixture required for each experiment is quite small since it is usually only necessary for the solvent to diffuse 2—3" past the test patch on the paper strip.

Effect of Other Ions on the Detection of Uranium.—Interference due to the presence of other metals has not proved serious. Thorium is partly extracted by the solvent mixture, particularly when the concentration of nitric acid is high (10%), and moves with uranium, but the presence of this element does not alter the subsequent colour test with potassium ferrocyanide. Large amounts of phosphate ion, as already stated, must be complexed with ferric nitrate, but the test can be carried out in the presence of moderate quantities of chloride, sulphate, oxalate, and acetate providing a high concentration of nitrate ion is present in the solution to be tested. Ferric salt is extracted if chloride is present, but movement is slower than that of uranium and a clear separation into two bands due to these elements can be achieved. The exact amount of anions other than nitrate which can be tolerated has not yet been fully established but the methods described for preparation of samples have been found adequate to cope with a very wide range of materials. The effect of anions will vary to some extent with the solvent and proportion of nitric acid used, but with 2-methyltetrahydrofuran and tetrahydropyran, which have been employed in this work, the results have been very satisfactory.

Results and Conclusions.—A number of minerals and ores have been examined by the method described above, with results summarised in the table, and compared with values obtained by standard methods of chemical analysis. In view of the small quantity of material involved in the analyses and the speed of operation, the agreement is reasonably good, and the method has proved of great convenience in exploratory and control work.

U as % U ₃ O ₈ by standard methods.	U as % U ₃ O ₈ by chromatographic technique : by visual comparison of ferrocyanide stain.	U as % U ₃ O ₈ by standard methods.	U as % U ₃ O ₈ by chromatographic technique : by visual comparison of ferrocyanide stain.	U as % U ₃ O ₈ by polarographic determination.
1.30	1.2	0.039	0.05	—
0.56	0.45	0.035	0.04	—
0.34	0.30	0.008	0.005	—
0.33	0.25	1.26	—	1.16
0.36	0.32	0.31	—	0.30
0.11	0.1	0.69	—	0.70
0.03	0.03	0.91	—	0.94
0.02	0.03	1.33	—	1.25

Much larger quantities of uranium than 200 μ g. can be dealt with by replacing the paper strip or sheet with tubes packed with cellulose. This application to quantitative analysis of uranium has been fully developed by Mr. R. A. Wells and others in this Laboratory and will form the subject of another communication.

Regarding the mechanism underlying separation of uranium by this combination of solvent extraction and solid absorbents, a number of factors have to be taken into consideration : (a) the high solubility of uranium in organic media under specific conditions which in all probability involves complex formation with the solvent, (b) the adsorption of other metals by the cellulose whereas uranium is not adsorbed to an appreciable extent under the conditions of the experiments, and (c) the partition of inorganic substances between solvent and water, including the water present in the absorbent paper strip. All of these factors appear to play a part in the separation process and such fundamental aspects are at present under investigation. It is clear, however, that chromatographic methods, of which this is one example, have a very wide application to inorganic analysis.