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 Reports, Department 4270, September, 1956
 TO: See Distribution Below
 FROM: C. D. Susano

The abstracts of the Preliminary Reports that were issued from the Analytical Chemistry Division, Department 4270, during September, 1956, are presented in this report. A subject index is also included in this compilation.

Any opinions or conclusions, which are expressed in these abstracts, are tentative and subject to revision or correction before they are issued in more formal reports. Comments, suggestions, and criticisms of this material are solicited.

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AUTHOR INDEX AND ABSTRACTS OF PRELIMINARY REPORTS

DEPARTMENT 4270

SEPTEMBER, 1956

R. G. Ball

Spectrophotometric Method for the Automatic Titration of Fluoride, RGB-36

The Warren Spectracord was applied to the automatic titration of 5 to 35 μ g of fluoride with thorium nitrate with a coefficient of variation of four per cent when alizarin red-S was used as the indicator. Preliminary tests made on other possible indicators for the titration, which included Thoron, carminic acid, chloranilic acid, and quercetin, revealed that quercetin was the only compound that was tested, other than alizarin, with which well-defined titration curves were achieved. Reproducible results of the end point in the titration of fluoride with thorium in the presence of quercetin, however, were not accomplished.

L. J. Brady

Comparative Costs of the Spectrophotometric and X-Ray Absorption Methods for the Determination of Uranium, LJB-16

The costs of the determination of uranium by the spectrophotometric, thiocyanate-ethyl acetate method and by X-ray absorption were estimated and compared. These costs were divided into five categories: labor, equipment, supplies, maintenance supplies, and contingencies. It was estimated that the costs of the determination of uranium by the spectrophotometric method and the X-ray absorption method were 2.70 and 3.00 dollars per sample, respectively.

Fluorometric Determination of Uranium, LJB-17 and RLM-23

When the reproducibility of results for the fluorometric determination of uranium, as estimated from the duplicate determinations of samples from the Pilot Plant, and from the repetitive analysis of a standard sample, was compared, the precision for the two sets of data was found to be essentially the same. The variation in duplicate determinations, then, is considered to be commensurate with the precision that is associated with the replicate analysis of a standard sample.

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J. R. French

Determination of Carbon Monoxide in Acidic Solutions of Cuprous Chloride, JRF-6 and 7

JRF-6: In a continuation of the study of the estimation of carbon monoxide, a determination of the palladium metal which is formed by the reaction of palladous chloride with carbon monoxide was investigated. The palladium metal was removed from solution by filtration; then the residue was dissolved in nitric acid prior to the colorimetric determination of palladium by means of the alpha-furildioxime method. It was found that some univalent copper remained with the palladium during the separation step; therefore, hydrogen peroxide was added to the final test solution prior to color development in order to remove the interference of cuprous copper. In general, the results that were obtained in the determination of known amounts of carbon monoxide by this proposed method were high and erratic.

JRF-7: In a further attempt to determine carbon monoxide in acidic solutions of cuprous chloride by a reaction with palladium, the palladium metal was removed from solution by filtration and then dissolved in a mixture of hydrochloric acid and hydrogen peroxide prior to the colorimetric determination of the metal. The results of the determination of known amounts of carbon monoxide by this method lacked precision.

Comparison of a Multichannel Flame Spectrometer With a Beckman Flame Spectrophotometer, JRF-8

In this report, the results which were obtained for calcium in the presence of sodium and potassium by means of both a flame spectrometer and a Beckman flame spectrophotometer were compared. The multichannel spectrometer had been modified for automatic background correction. It was found that the interference of either sodium or potassium in the determination of calcium is much less when the spectrometer is used as the means of measurement. The addition of an instrument, such as the multichannel spectrometer, to the analytical laboratories would be desirable.

T. W. Gilbert, Jr.

The Determination of Oxygen in NaK by the Butyl Bromide Method, TWG-1

A buffering effect in the pH region of 4 to 7 has been frequently observed in the determination of oxide in NaK by means of the butyl bromide method. From an investigation of the cause of this effect it was found that traces of aluminum in the NaK are most likely responsible. The presence of small amounts of aluminum should have little effect on the accuracy of the titration, however.

C. A. Horton

The Determination of Trace Amounts of Molybdenum, CAH-9

Previous studies have shown that vanadium interferes in the colorimetric method for the determination of molybdenum when butyl acetate is used as the extractant. In the literature, a selective extraction of molybdenum 8-quinolinolate in chloroform at a pH of 0.9 to 2.1 without interference from aluminum, copper, iron (III), nickel, titanium, uranium (VI), or vanadium (V) is described. Similar experiments in this laboratory indicate interference of both vanadium (V) and (IV) in the estimation of molybdenum at a wavelength of 570 m μ at pH ranges between 1 and 2.2. Further, the absorbance index of the molybdenum 8-quinolinolate is not very high. The absorbance of nine μ g of vanadium was equivalent to that of 1 μ g of molybdenum.

Method for the Direct Estimation of Uranium, CAH-10

Uranium, thorium, and zirconium, when extracted into triocetylphosphine oxide in cyclohexane from a nitric acid solution, are not present as tightly bound complexes. These elements, however, form colored complexes with chelating compounds. Morin produces a green fluorescence with either zirconium or thorium, but gives only a yellow color with uranium. Less than 0.5 μ g of uranium/ml can be detected in this colored solution. Benzoylacstone gives a yellow color with uranium, but none with thorium or zirconium. From these observations, possibilities of analytical methods for the determination of thorium or zirconium and for uranium are suggested, since very few substances extract into triocetylphosphine oxide from a solution of nitric acid.

E. C. Lynn

Lithium Content of Nickel Foil, ECL-8

The lithium content of two samples of nickel foil was determined. After the samples were rinsed in dilute acid, they were found to contain 80 to 410 μ g of lithium, respectively. Very little lithium was detected, by a flame photometric method, after the entire foil was dissolved in nitric acid.

M. A. Marler

Outline of the Semiannual Progress Report, Analytical Chemistry Division, MAM-22

The work which was described in the Semiannual Progress Report, Analytical Chemistry Division, Department 4270, for the Period Ending April 20, 1956 was outlined in order to present the status of the projects of this division. The projects are divided into sections of initiated, completed, and continued work, as based on the work and status of reports which pertain to the projects.

R. L. McCutchen

Fluorometric Determination of Uranium, RLM-21 thru 23, 28, 42 thru 44

RLM-21: The effect of certain extraction conditions on the fluorescent intensity of uranium phosphors and on the reproducibility of fluorescent measurements was investigated. The intensity of the phosphors and the reproducibility of the measurements were found to be unaffected by the conditions of extraction that were studied.

RLM-22: The effect on the intensity of the fluorescence of uranium phosphors of using glassware that had been cleaned mechanically was investigated. The use of the mechanically cleaned glassware was not considered to have a deleterious effect on the intensity of the phosphors.

RLM-23: See LJB-17

RLM-28: This study was initiated to evaluate the reproducibility of fluorescent measurements within and between days, so that the practicality of a daily calibration factor for the fluorometric determination of uranium could be ascertained. Unless 25 to 50 per cent of the measurements were rejected, the reproducibility of the data within and between days was found to be essentially the same; consequently, the use of a daily calibration factor is not recommended unless the erratic measurements can be minimized or eliminated.

RLM-42: In an effort to improve the reliability of the fluorometric method for the determination of uranium, a new Photovolt fluorophotometer (Y-117,449) was substituted for a similar instrument (Y-92,635) which has been in use for some time in Room 7 of Building 9733-4. The reproducibility of the fluorescent measurements on this new instrument was found to be about 15 per cent as compared to 20 per cent for the older fluorophotometer.

RLM-43: Preliminary tests were made to determine the feasibility of preparing uranium phosphors in a muffle furnace at 800°C. It was found that satisfactory phosphors can be prepared in this manner.

RLM-44: An evaluation of calibration data for a batch of flux, prepared on August 27, 1956, was made to establish the reproducibility of the calibration factor for the fluorometric determination of uranium. The variation in the factor was found to be about 15 per cent, which is essentially the same as the reproducibility of the factor for an older batch of flux, prepared on August 8, 1956; consequently, substitution of the newer batch of flux for the older one is not expected to affect the precision of the fluorometric method for the determination of uranium.

Determination of the Amine Content of Samples from the Pilot Plant,
RLM-24, JMP-12

The possibility of making a single analysis, instead of duplicate determinations, of the amine content of samples from the Pilot Plant was investigated. Since the variation "within" days was less than that "between" days, the use of a single determination is apparently sufficient.

Volumetric Determination of Uranium, RLM-25 and 37

RLM-25: Uranium values which were secured by two volumetric methods were compared to justify the substitution of the zinc-ceric sulfate method for the automatic titrator-potassium dichromate procedure. This substitution was found to be justified.

RLM-37: A standard sample of UO_3 (NBL No. 18) was provided for use as a primary standard in establishing a titer for a solution of ceric sulfate which is an integral part of the volumetric method for the determination of uranium. The titer, established for this solution of ceric sulfate, is 2.25×10^{-3} g/ml.

Analysis of a Sample of UO_3 , RLM-33 (See CDS-9)

A sample of UO_3 , designated NBL No. 18, was analyzed in cooperation with the New Brunswick Laboratory to establish the composition of this material so that it can be used as a basis for an AEC standard. Although the composition has been established, in this department, a comparison with the results of other laboratories is now being made at NBL; therefore the sample is not available for use as an AEC standard at this time.

Spectrophotometric Determination of Uranium, RLM-41

Experiments similar to those reported in RLM-38 were repeated to determine the degree of reproducibility that is attainable for the determination of uranium by the ammonium thiocyanate-ethyl acetate method when the preparation temperature of the chromogenic reagent is controlled. The precision for this method of analysis was found to increase by a factor of two, or from ten to five per cent, when this variable was controlled.

B. M. McDowell

Spectrophotometric Determination of Niobium, BLM-56

The method of Ward and Marrazzino for the spectrophotometric determination of niobium was adapted for use in this laboratory. The absorbancy of niobium is measured as the thiocyanate complex at a wavelength of 387 mμ. At this wavelength, a linear relationship exists between absorbance and concentration of niobium from 0.5 to 3.0 μg/ml of niobium. The coefficient of variation of the method is approximately five per cent.

J. M. Peele

Determination of Amine Content of Samples From the Pilot Plant, JMP-12 and RLM-24

See RLM-24

W. J. Ross

Extraction of the Elements with Trioctylphosphine Oxide From Acidic Solutions, WJR-106-109, 111-114

WJR-106: In a continuation of the study of the extraction of different elements into trioctylphosphine oxide (TOPO), the effect of type and concentration of acid on the extraction of ferric and ferrous iron was determined. It was found that neither ferric nor ferrous iron is extracted from solutions of sulfuric acid or phosphoric acid. In addition, ferric iron is not extracted from aqueous phases that contain nitric acid; however, trivalent iron can be extracted from hydrochloric acid, particularly 7 to 10 M solutions. Through variations of acid type and concentration, therefore, ferric iron can be extracted into cyclohexane solutions of TOPO or retained in the aqueous phase during the extraction of other ions.

WJR-107: In the extraction of zirconium into TOPO from various acidic solutions, it was found that ten mg of zirconium can be extracted from 1 to 10 M solutions of hydrochloric or sulfuric acids. The amount of zirconium which is extracted from nitric acid is dependent on the concentration of the acid in that, as the concentration increases, the amount of zirconium that is extracted also increases. A white solid formed when 1, 4, and 10 M solutions of phosphoric acid were mixed with zirconium.

WJR-108: After the effect of acid type and acid concentration on the extraction of zirconium into TOPO was established, the effect of reagent concentration was determined. It was found that the amount of zirconium that is extracted is a function of the concentration of TOPO. The molar ratio of the complex in the organic phase is two, thus indicating that one mole of zirconium in hydrochloric acid is extracted into cyclohexane solutions with two moles of TOPO.

WJR-109: It was also desirable to determine the effect of reagent concentration on the extraction of ferric iron into TOPO. The amount of iron that is extracted is a function of the concentration of TOPO. The molar ratio indicates that Fe^{+3} is extracted into the organic phase as $\text{Fe}^{+3} \cdot 2\text{TOPO}$.

WJR-111: The effect of concentration of ferric iron on the extraction of this material from 7 M HCl into cyclohexane with 0.1 M trioctylphosphine oxide was determined. As much as ten mg of iron is quantitatively extracted by 0.5 millimoles of the phosphine oxide. The same quantity of reagent is loaded when 15 mg of trivalent iron is extracted.

WJR-112: The effects of various experimental conditions on the extraction of ferric iron from chloride solutions with trioctylphosphine oxide (TOPO) were determined. The loading capacity of 0.5 millimoles of TOPO was not changed when the equilibration time was varied from 10 to 20 minutes. A small but continuous decrease in the extractability of iron occurs when the phase ratio, V_o/V_a , is varied between 1 and 0.25. Practically no iron is extracted into TOPO from solutions of pH ≥ 0.3 .

WJR-113: The spectra were determined for the organic phases that were obtained when ferric iron was extracted from HCl solutions into cyclohexane with trioctylphosphine oxide. Two maxima were found for systems that included 1 to 9 M HCl. The magnitudes of the maxima and the wavelengths differ to such an extent in 1 M and 2 to 9 M media that two types of complexes are indicated. The molar extinction indices of 2 to 9 M systems are comparable to that of the ferrous iron-orthophenanthroline complex.

WJR-114: A preliminary survey is presented of the applicability of the tri-n-alkylphosphine oxides for the analytical separation of elements by solvent extraction. The experimental work was undertaken to ascertain which substances can be extracted into the phosphine oxides in order that a cursory observation on the possible uses of these oxides as analytical extractants can be made. The qualitative data that were collected indicate the degree of extraction and the best acid media for the extraction.

C. D. Susano

Cooperative Analysis of a Standard Sample of UO_3 , CDS-9 (See RLM-33)

A summary of the results and methods of analysis of a standard sample of UO_3 , designated as NBL-18, is presented in this report. The analyses were made as a part of the cooperative program which is being conducted by the New Brunswick Laboratory. A report of these results has been sent to NBL for study and evaluation with the data from other laboratories.

W. F. Vaughan

The Volumetric Determination of Uranium, WFV-2 and 3

WFV-2: See RLM-25

WFV-3: See RLM-37

J. C. White

Chemical Analyses of Samples from Wright Air Development Command, JCW-53

A total of 12 samples from WADC were analyzed to determine the amount of zirconium, uranium, nickel, iron, and chromium that was present. Three additional samples were analyzed for hydrogen content.

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ANALYTICAL CHEMISTRY DIVISION

DEPARTMENT 4270

SEPTEMBER, 1956

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