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TO: R. E. Curtis

The monthly meeting of the Analytical Development Group with Dr. H. H. Willard was held August 19 and 20. Principally, the determinations of uranium and aluminum in Redox streams and the determination of trace impurities in calcium were discussed.

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## MINUTES OF MONTHLY MEETING WITH DR. H. H. WILLARD

August 19-20, 1948

## I. DETERMINATION OF ALUMINUM IN REDOX STREAMS

### a. Method in Control Laboratory Use

The titrimetric oxine procedure was modified such that a 10-30% oxine excess based on the aluminum requirement alone is used. By eliminating the oxine which would be required by the uranium present, a much easier separation of aluminum was effected. Samples with a UNH/ANN ratio as high as 150 were run successfully. When iron and chromium are present a perchloric acid fuming, a mercury cathode electrolysis, and a second perchloric acid fuming to oxidize uranium, and residual chromium to the hexavalent states are employed. Accuracy is satisfactory; however, the procedure is time consuming.

### b. Iron Complexing Method

Following a perchloric acid fuming to oxidize chromium to the dichromate state, the sample is made weakly alkaline with saturated ammonium carbonate in the presence of tartaric acid. The sample is warmed to 70° and potassium cyanide added followed by the addition of 10-30% excess oxine based on the aluminum requirement. Results are about 1-2% high, although better accuracy appears to be forthcoming. Dr. Willard indicated that the ferrocyanide complex is to be desired because of its greater stability.

### c. Ion Exchange Separation

The basis for the separation of aluminum from other cations appears in an article, Luré and Filoppona "Zavodskaya Lab.", 13 539 (1947) (C.A. 4484, July 10, 1948). The isolated aluminum is determined by the titrimetric oxine procedure.

### d. Acidimetric Titration of Aluminum

The basis of the procedure is described in the February, 1948 issue of "Analytical Chemistry". Other cations are separated from aluminum by sodium hydroxide precipitation. Accuracy has not been satisfactory. Dr. Willard suggested that the quantitative separation of aluminum from other cations in sodium hydroxide solution is difficult to accomplish. The results of an extensive literature survey by Rodden indicate that the following organic reagents may be useful for the separation of $U^6$ and $Fe^3$.

1. quinoldic acid
2. 1. nitrose, 2 naphthol
3. tannic acid
4. insatin ∕ oxime

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e. Aluminum in Hexone

The hematoxylin method is subject to error in the presence of iron. Dr. Willard suggested the reduction of iron, complexing iron with orthophenanthroline, and a permanganate oxidation to the ferricomplex which is faintly blue. If the oxidized complex is sufficiently stable, a reliable aluminum determination may be possible.

f. Conductometric Titration of Aluminum

The oxine titration was mentioned.

## II. THE DETERMINATION OF ALUMINUM IN WATER

An aluminum determination is necessary for water containing 0.02 - 0.04 p. Fe p.m. and 0.004 p. Al p.m. The hematoxylon method lacks sensitivity and is subject to iron interference. The iron interference may be eliminated possibly by oxidation of the O-phenanthroline complex. Aluminum may then be determined colorimetrically with aluminon or morin, or fluorimetrically with quantichrome blue black. As a reducing agent for iron $Na_2S_2O_4$ was suggested; although, an excess should be avoided to prevent formation of a large quantity of free sulfur.

## III. APPROXIMATE UNH DETERMINATION

The polarigraphic procedure appears to be rapid enough for application. Hydrazine is added to reduce iron and dichromate and the titration is carried out in a supporting electrolyte consisting of 150 g ANN/l, 0.1 N HCl, $Cr^{+++}$, $Fe^{++}$, hydrazine and $HNO_3$. Precision has not been satisfactory. Dr. Willard indicated that a nitric acid-hydrochloric acid reaction may be causing erratic results. The possibility of current integration was mentioned. The fact that the half wave potential becomes more negative with increasing UNH concentration was brought out. Dr. Willard plans to discuss the matter with Dr. Furman.

## IV. FLUORIMETRIC DETERMINATION OF UNH

The method is being applied to 0.01 γ uranium. Dichromate quenching is being investigated. Precision is not satisfactory. Dr. Willard suggested that a Ag Cl - Na F flux might be workable and quite advantageous in eliminating cracking of the bead during cooling. Nitrate, if present, would decrease the clarity but could be removed with chlorine gas.

Dr. Willard mentioned the use of electrolytic deposition of uranium from a neutral oxalate solution, as done at Argonne, with subsequent counting may have analytical value. Dr. Pearce stated that such is being done at K-25.

## V. COLORIMETRIC UNH

The thiocyanate method is not reliable.

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VI. DETERMINATION OF NITRIC ACID

At the monthly Redox meeting in Schenectady, the following was decided:

1. The modified (4° C) oxalate method is the most accurate.

2. The KF method is satisfactory but depends on the quality of the KF.

3. The KF method may be satisfactory for the IDP column if ANN is used.

VII. CONDUCTIMETRIC TITRATION OF AcOH AND $HNO_3$ IN HEXONE

Dr. Willard indicated that he will submit a list of necessary equipment. The use of an AC vacuum tube voltmeter for null point determination was discussed.

Substituted ammonias were suggested for titrating weak acids.

VIII. VOLUMETRIC UNH ($Cr^{++}$ - $Fe^{+++}$ TITRATION)

No work was done. A stock supply of platinum electrodes in strong oxidant will be introduced.

IX. VACUUM DISTILLATION OF $HNO_3$

The cake, after cold distillation, is treated with water and the water distilled at 70° C. The $HNO_3$ recovery is 89%. Repeated warm distillations will yield 100% recovery.

X. BORON

The method has not been appreciably changed. Corning resistance glass and silica sample crucibles are used. Up to 2 g $NaNO_3$ tended to cause flashing of methyl alcohol, whereas no such effect was observed when $Ca(NO_3)_2$ was used.

The excess acid factor as it occurs with the use of nitric acid could be eliminated by substituting phosphoric acid.

Dr. Willard donated spectrophotometric curves from G. H. Ellis. The feasibility of the following boron colorimetric reagents was indicated:

1. 1, 1-dianthrimide (used in $H_2SO_4$)

2. Quinalizarin

The first fluoresces in a convenient range.

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## XI. FLUORIDE DISTILLATION

Fluorine is being determined with para di methyl amino azo phenyl arsonic acid. A 25% solution in alcohol-hydrochloric acid (9:1) is heated to 60°, agitated, added slowly to 1% zirconium oxychloride in 1 N HCl, and agitation at 60° continued for 12 hours. The residue is ground with sand.

Dr. Willard suggested the use of a protective colloid.

The suggestion was made to distill into the zirconium oxychloride solution, to react with the free acid, and finally to water extract the colored substance which would be formed if fluorine were present.

The large nitric acid excess may be destroyed by electrolytic reduction or ferrous sulfate reduction with a molybdenum catalyst.

The presence of $Fe^{+++}$ and $Al^{+++}$ increases the required distillation time considerably in order to break up corresponding fluorine complexes.

## XII. DETERMINATION OF $FE^{+++}$ IN IBP

A large excess of $Fe^{++}$ is present. Potassium thiocyanate may work satisfactorily; although, nitric acid will probably give a color. 4 hydroxydiphenyl carboxylic acid has not been obtained.

## XIII. WATER IN HEXONE

Modified (reduced amount of methyl alcohol) Karl Fischer reagent is being used. High UNH samples give a precipitate (excess pyridine dissolves it) which obscures the end point. Hydrazine and possibly ferrous sulphamate reduces iodine.

In the direct titration of water by the reagent methyl alcohol produces an error. The use of isopropyl or butyl ethers was suggested. The dead stop end point is satisfactory.

## XIII. DETERMINATION OF HEXONE IN WATER

The present method involves a distillation of the hexone followed by the iodiform reaction and titration with sodium thiosulfate.

The primary reaction is such that 1 mole of hexone reacts with 6 moles of iodine; although, high recoveries indicate that a secondary reaction occurs in which 10 moles of iodine are consumed. The method is set up on an emperical basis. A 100 λ sample containing 0.8 mg. hexone gives 1-3% error.

## XIV. DETERMINATION OF METHYL ISOBUTYL CARBINOL

No further work has been done. A colorimetric procedure might be worked out if a colored acid could be found to produce a colored ester.

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## XV. DETERMINATION OF AMMONIUM NITRATE IN THE PRESENCE OF HYDRAZINE

The oxidation of hydrazine followed by the distillation of ammonia has not been investigated.

## XVI. SPECIFIC GRAVITY

The falling drop method appears to be the only one applicable to radioactive solutions. An accuracy of 20 ppm is indicated. A rising drop for the hexone phase may be possible.

## XVII. STANDARD REDOX SAMPLES

Dr. J. F. Flagg, Schenectady, is consulting with the National Bureau of Standards to establish samples to be run on all sites.

## XVIII. DETERMINATION OF TRACE IMPURITIES IN CALCIUM

No difficulties have been encountered in the determination of Mn, Fe, Cl, and $N_2$.

Aluminum (10-150 ppm). Present method (glass bead absorption followed by hematoxylin method) gives fairly good results. The use of quartz beads instead of glass to prevent the possibility of interference by the aluminum present in glass has been suggested. Procurement of quartz beads is a problem, however. Hanford Works Al values are high compared to the average value from other analytical laboratories. M.I.T. values (obtained spectrographically), however, were comparable. Calcium interferes in the direct determination of aluminum using the hematoxylin method. Aluminum and alizarin colorimetric methods were suggested. A fluorescence method using morin (yellowish green) was also suggested. Iron would first have to be complexed by o-phenanthroline with a hydrosulfide reductant. A Pontachrome fluorescence method (orange-red) would probably also be satisfactory. (C. S. Lowe of the Research Section is co-author with C. E. White of the University of Maryland of several articles on fluorescence methods for the determination of aluminum).

Chromium (1-10 ppm). Calcium interferes in the direct determination of chromium using the diphenylcarbazide colorimetric method. The use of glass bead absorption of chromium as a separation from calcium seems promising.

Copper (10 ppm). Calcium and iron were found to interfere in the use of the sodium diethyldithiocarbamate colorimetric method for copper. The rubeanic acid method, using malonic acid as complexing agent, will be attempted as soon as all the reagents are procured.

Cobalt (1-10 ppm). Iron seems to interfere in the tetraphenylarsonium chloride colorimetric method. Also, this method may not be sensitive enough to determine cobalt at such low concentrations. A method in which the cobalt is complexed with excess thiocyanate and extracted into

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ethyl acetate was recommended as a more sensitive method. Iron interference can be eliminated by reduction with stannous chloride.

Nickel (1-10 ppm). Some difficulty caused by turbidity has been found in the use of the dimethylglyoxime method for nickel. In this method, bromine is used as the oxidizing agent. With the pH adjusted to 9.0-9.5, carbon dioxide was suggested as causing the turbidity. Solvent extraction of the color was suggested as a possible remedy.

Magnesium (500 ppm). The titan yellow method was suggested as the most promising method for the determination of magnesium. Aluminum interference might be removed by adding excess alkali to form the aluminate. Calcium is known to have an intensifying effect on the color. Gum arabic or gelatin could be used to stabilize the precipitate formed. Sample size may be critical.

Silicon (50 ppm). The gravimetric fluoride method was found to be not sufficiently accurate at such low silicon concentrations. A molybdate method based on a July, 1948 article appearing in "Analytical Chemistry" has been tried, but no color development was obtained. Formation of colloidal silica was suggested as the cause. To remedy this effect, the $SiO_2$ solution could be made more alkaline, stannous chloride added, and then the solution made acid rather than completely acidifying before reduction.

## XIX. ANALYSIS OF SPECIAL GAS SAMPLE

A 250 cc sample of gas evolved from a 1 gram sample of neutron-irradiated magnesium oxychloride has been submitted for analysis for $O_2$, $H_2$, $N_2$, $Cl_2$, $H_2O$ vapor, HCl vapor, and other gases. Normal gas analytical methods could be used for $H_2$ and $O_2$. Chromous chloride ("Oxorbent") was suggested to be used instead of alkaline pyrogallol for the determination of oxygen.

Chlorine. Difficulty has been encountered in determining chlorine by solution in water and using the tolidine colorimetric method. Acidification was suggested as an aid in preventing chlorine hydrolysis while using this method. Other suggested methods include absorption in standard arsenite solution or in buffered (boric acid-borate) potassium iodide solution.

Water Vapor. By passing the gas through anhydrone, water vapor could be determined by the increase in weight of the absorbent.

Nitrogen. A suggested method for nitrogen would be to absorb the nitrogen in magnesium to form the nitride, then hydrolyze to ammonia and determine the ammonia.

## XX. DETERMINATION OF NaCl IN HCl

A flame photometer, or spectrographic method was suggested for use in this analysis.

## XXI. DETERMINATION OF PHOSPHORUS AND MAGNESIUM IN URANIUM AND URANIUM OXIDE

Wet chemical methods are needed to verify high spectrographic findings.

**Phosphorus.** A molybdate colorimetric method (H. W. Manual, Ion Methods HSP-1a) in which molybdiphosphoric acid is reduced with stannous chloride and the resulting blue color is extracted into n-butanol out of a 1N $H_2SO_4$ solution was suggested for the determination of phosphorus.

**Magnesium.** A concentration method in which the uranium was ether extracted followed by a colorimetric (titan yellow) determination was suggested for magnesium. If UNH would interfere in the titan yellow method, one of F. Feigl's magnesium methods in which a blue color is developed could be attempted.

## XXII. DETERMINATION OF SMALL AMOUNTS OF URANIUM IN Al-Si, TIN AND BRONZE

**Tin.** Volatilization of Sn using an HCl-HBr mixture could be used to remove the Sn and concentrate the uranium. Dry chlorine could also be used to volatilize the tin.

**Bronze.** Electrolytic removal of Cu and Sn using a hydrochloric acid solution with an anodic depolarizing agent, such as $H_2NOH$, could be used to concentrate the uranium. A Pt-Ir anode would also help in the electrodeposition of Cu and Sn.

**Al-Si.** Volatilization of Al and Si with dry chlorine would leave a concentrated uranium residue for analysis.

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