

CC-1432  
(A-2263)

Metallurgical Project

A. H. Compton, Project Director

...

✓ Clinton Laboratories

M. D. Whitaker, Director

R. L. Doan, Associate Director for Research

...

ANALYTICAL DIVISION

D. M. Smith, Division Director

...

PROGRESS REPORT

DETERMINATION OF FREE NITRIC ACID IN UNH SOLUTIONS

PROBLEM ASSIGNMENT NO. 208-X2A

April 21, 1944

Experimental Work By: C. W. Hammond  
Submitted By: A. K. Parlour, Group Leader  
Approved By: M. R. Hoff

Received Clinton: 4/21/44  
Series A Issued: 4/22/44  
Received Chicago: 4/26/44  
Series B Issued:

JUN 9 1944

Photostat Price \$ 1.80  
Microfilm Price \$ 1.80  
Available from the  
Office of Technical Services  
Department of Commerce  
Washington 25, D. C.

CLASSIFICATION CANCELLED  
DATE 12/12/77  
For The Atomic Energy Commission  
H. A. Canale  
Chief, Classification Branch

860-1

ABSTRACT

Since UOH is a highly dissociated compound which ionizes to  $\text{NO}_3^-$  and  $(\text{UO}_2)^{++}$ , the latter ion being very weakly basic, a solution of pure UOH is quite acid (pH about 3). It is possible to titrate to a phenolphthalein end point with standard caustic solution and obtain a figure which represents the free acid plus the  $\text{NO}_3^-$  from the UOH. However, the titration of the free nitric acid alone in such a solution presents quite a problem.

By precipitating and removing uranium from solution by means of potassium ferrocyanide, the residual free acid may be titrated directly by means of standard caustic using either methyl red or phenolphthalein indicators, with an error of less than 1%. A method is given to determine formic acid, should that acid be present in the mixture.

866-2

This document contains information affecting the national defense of the United States within the meaning of the Espionage Act, Title 18, U.S.C., Sec. 793 and 794, and the transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

### INTRODUCTION

The methods in use at site X to date are (1) a potentiometric method developed by the semi-works group, and (2) the peroxide method described in CE-367. The potentiometric method uses a Beckman pH meter to indicate the end-point of the titration of the free acid with standard caustic. The "break" which occurs at about pH 2.5 to 3.2 supposedly represents the stoichiometric point of the free acid. When titrated in this manner, a 1 ml. sample of UNH in about 30 ml. of water gives a  $\Delta$  pH of about 0.15 for about 0.25 ml. of N/3 NaOH, and a total titration of about 3-4 ml.

In the second method, the uranium is precipitated as the peroxide and the total acid remaining is titrated. The uranium is then determined and the nitric acid equivalent calculated. The difference between the total acid and the nitric acid equivalent of the uranium is the free acid in the sample.

In the proposed method, the uranium is precipitated from the solution as an insoluble precipitate, and the  $\text{NO}_3^-$  left as a neutral salt (e.g.  $\text{KNO}_3$ ). The excess nitric acid which represents the free acid in the sample may then be titrated directly using an ordinary indicator. Since potassium ferrocyanide is used as a quantitative precipitant in the determination of uranium, this was chosen as a likely precipitating reagent.

### EXPERIMENTAL

Mallinckrodt reagent grade UNH was doubly recrystallized from distilled water in an effort to obtain acid free UNH. A 20% by weight solution of this was made up and used for all the preliminary work. 1 ml. samples of this solution were pipetted into 25 ml. volumetric flasks and diluted to about 10 ml. with saturated  $\text{KNO}_3$  solution which had been neutralized to methyl red with N/10 NaOH. To these were added 0, 1, 2, 3, 4, and 5 ml. of standard nitric acid solution (0.1544 N.). Then 5 ml. of a solution of potassium ferrocyanide (5 gm.  $\text{K}_4\text{Fe}(\text{CN})_6$  in 100 ml. saturated  $\text{KNO}_3$  solution.) were added to each flask and the volume made to the mark with saturated  $\text{KNO}_3$  solution. After thorough shaking, about 20 ml. were placed in 20 ml. lusteroid tubes and centrifuged for 10 minutes at 3000-3500 r.p.m. in a No. 2 International centrifuge. 15 ml. of the clear super-

860-3

stant were pipetted into small flasks, diluted with water and titrated with N/10 NaOH. to Methyl Red end-point. On other mixtures containing only nitric acid and saturated  $\text{KNO}_3$ , the presence of the salt was found to have no effect upon the stoichiometric end-point. The presence of the potassium ferrocyanide likewise had no effect upon the end-point.

In the following table, the nitric acid has been calculated to per cent to simulate a plant sample of 1 ml. of the 20% UNH solution.

TABLE I

## RECOVERY OF NITRIC ACID ADDED TO PURE 20% UNH SOLUTIONS

| Effective<br>milli-<br>equiv.<br>$\text{HNO}_3$ added* | Milli-<br>equiv.<br>NaOH<br>used | Milli-<br>equiv.<br>difference | Per cent<br>difference | Per cent<br>$\text{HNO}_3$<br>added | Per cent<br>$\text{HNO}_3$<br>found |
|--|----------------------------------|--------------------------------|------------------------|-------------------------------------|-------------------------------------|
| 0.0000   | 0.005                            | 0.005                          | --                     | 0.00                                | 0.04                                |
| 0.0926   | 0.103                            | 0.010                          | 10.8                   | 0.55                                | 0.94                                |
| 0.1852   | 0.192                            | 0.007                          | 3.6                    | 1.69                                | 1.75                                |
| 0.2778   | 0.275                            | 0.003                          | 1.1                    | 2.54                                | 2.52                                |
| 0.3704   | 0.367                            | 0.003                          | 0.8                    | 3.38                                | 3.36                                |
| 0.4630   | 0.467                            | 0.004                          | 0.9                    | 4.23                                | 4.26                                |

\* allowing 3/5 of total acid added in aliquot taken.

Nine plant runs were analyzed by this method and the results compared with the results obtained from the electrometric method using the Beckman pH meter. In this latter method, the sample is titrated in 0.2 ml. increments to the point of greatest inflection. Thus the exact titration is known only to the nearest 0.2 ml. and frequently may not be known but to the nearest 0.4 ml. if two successive increments give equally great inflection. An uncertainty of 0.2 ml. in 2.5 ml. titration (equivalent to about 3%  $\text{HNO}_3$  in a 1 ml. sample) gives an uncertainty of about 10%, while on a 0.8 ml. titration (equivalent to about 1%  $\text{HNO}_3$ ) the uncertainty is nearly 40%.

860-4

TABLE II

COMPARISON OF PERCENT FREE NITRIC ACID AS OBTAINED BY  
POTENTIOMETRIC TITRATION AND BY PRECIPITATION TITRATION

| Run No. | Potentiometric      | Precipitation        | Difference |
|---------|---------------------|----------------------|------------|
| 30      | 2.0% $\text{HNO}_3$ | 2.10% $\text{HNO}_3$ | .10        |
| 31      | 1.6                 | 1.21                 | .39        |
| 32      | 2.7                 | 2.85                 | -.15       |
| 35      | 4.2                 | 4.94                 | -.74       |
| 36      | 2.4                 | 2.18                 | .22        |
| 37      | 1.5                 | 1.62                 | -.12       |
| 38      | 4.1                 | 4.41                 | -.31       |
| 39      | 0.4                 | 0.72                 | -.32       |
| 40      | 2.1                 | 1.91                 | .19        |

PROPOSED PLANT METHODSolutions

Saturated solution of  $\text{KNO}_3$ . 35 gm.  $\text{KNO}_3$ , 85 ml. water.  
Neutralize with N/10 NaOH  
to methyl red.\*

$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ . 5 gm. salt made to 100 ml. with saturated  
 $\text{KNO}_3$  solution.

Methyl Red Indicator 1 gm. / liter  
NaOH N/10 . 4.0 gm. / liter. Standardize.

Equipment

No. 1 or No. 2 International centrifuge.  
20 ml. Lusteroid tubes  
10 ml. burette  
25 ml. volumetric flasks  
15 ml. pipette  
Small beakers or flasks.

PROCEDURE

Add about 15 ml. of  $\text{KNO}_3$  solution and 3.0 ml. of potassium ferrocyanide solution (see note) to a 25 ml. volumetric flask. Add 1.0 ml. sample and shake vigorously for one or two minutes. Make to volume with  $\text{KNO}_3$

\* Use phenolphthalein if samples contain formic acid.

866-5

solution. Centrifuge about 20 ml. in 20 ml. tubes at 3000-3500 r.p.m. for 10 min. This is to settle most of the red precipitate and allow a supernatant clear enough to see the end-point. (A clinical centrifuge may be used if a longer time of centrifugation is used.) Pipette 15.0 ml. of the supernatant (being careful not to disturb precipitate) into a small beaker, dilute with about 50 ml. of water, add 2 or 3 drops of methyl red indicator (phenolphthalein when formic is present) and titrate to the color change which is quite sharp. Total time required about 20 min.

**NOTE:** The specified volume of ferrocyanide is sufficient to completely precipitate the uranium from 1.0 ml. of 20% UNH solution. However, should a more concentrated solution be under examination the sample size should be decreased rather than using more reagent inasmuch as the UNH concentration appears critical.

After the above method was worked out, an attempt to obtain an estimation of the acid from the pH of the supernatant solution was made. This was not successful due to the influence of excess precipitating reagent on the pH of the solution. Chart I shows the dependence of the pH upon the concentration of ferrocyanide solution.

#### CORRECTION FOR FORMIC ACID

Since the UNH solution may have formic acid in it (formic acid is used both to reduce and to consume excess nitric acid), the effect of formic acid on the method was investigated.

The question arose as to whether any formic acid would be left after reacting with free nitric acid in stoichiometric amounts in the presence of UNH. It was questioned whether due to the great dissociation of UNH solutions, free formic acid could react with the nitric formed from dissociation. Several samples were prepared from acid free UNH solution and varying amounts of formic acid added. These were then refluxed for two hours and allowed to stand over the weekend (about 50 hours). At the end of this time substantially all of the formic acid was recovered by analysis. On the basis of this information, it is assumed that small amounts of formic acid may be present after reaction, so such samples as have had formic acid added to them should be so tested.

As a preliminary work, it was found that formic acid could not be correctly titrated (as might be inferred) to a methyl red end-point, but nitric acid could be titrated to a phenolphthalein end-point that was not measurably different from that of methyl red. Other experiments showed that the presence of potassium ferrocyanide and of saturated solution of potassium nitrate did not effect the true end-point of the two acids to phenolphthalein. Then mixtures of formic acid and nitric acid were added to pure UNH solutions and the mixture run for total acid as in the above procedure.

P60-1

In each case, substantially 100% recovery was made, showing that if formic is present, it will be determined as nitric, when that determination is made.

In the determination of formic acid, use is made of the alkaline permanganate reaction, destroying excess permanganate with oxalic acid. (KI cannot be used since oxides of nitrogen which are present cause continuous liberation of iodine and a drifting end-point.) The oxides of nitrogen also use a little permanganate, so several UNH solutions were run for this oxide blank. This was found to run from 0.10 to 0.36 ml. N/10  $KMnO_4$  per ml. 40% UNH. If a 1 ml. 40% UNH contains 1.5% formic acid which uses about 6 ml. permanganate, the worst case found would introduce an error of only about 0.1% formic acid, so it is deemed that this can be neglected for production samples.

ANALYTICAL (FORMIC ACID)

Following is the method used: Make the sample alkaline with slight excess of sodium carbonate and add a measured excess of standard potassium permanganate. Heat to boiling and allow to stand about five minutes. Neutralize excess carbonate with 6 N. sulfuric acid and add 10 ml. excess. Titrate with N/10 oxalic acid until all permanganate color and all manganese oxides have disappeared. Heat to about 90° C. and titrate excess oxalic acid with permanganate. The color change is from a greenish yellow to a golden yellow and is fairly sharp. A blank solution of UNH for color comparison is helpful in determining the end-point.

Using the above method the following results were obtained:

TABLE III

RECOVERY OF FORMIC ACID ADDED TO UNH SOLUTIONS

| <u>Added Formic Acid</u> | <u>Found</u> | <u>Deviation</u> |
|--------------------------|--------------|------------------|
| 0.0134 gm                | 0.0146 gm.   | 0.0012 gm        |
| .0225                    | .0230        | .0005            |
| .0359                    | .0365        | .0006            |
| .0450                    | .0408        | .0042            |
| .0584                    | .0580        | .0004            |
| .0675                    | .0670        | .0005            |

The maximum deviation in this series is about 10% and this analysis might be expected to yield results of this order or better.

CALCULATION:

$$\text{Total acid (as } HNO_3) - 1.37 (\% HCOOH) = \% \text{ Free } HNO_3$$

860-7

EFFECT OF  $K_2Fe(CN)_6$  ON pH  
CHART 1

SYNTHETIC MIX

1 ML 20% UNH

1-5 ML 0.154 N  $HNO_3$

4-6 ML 5%  $K_2Fe(CN)_6$  MADE  
UP IN SATURATED  $KNO_3$

ALL SAMPLES DILUTED TO  
50 ML WITH SATURATED  $KNO_3$

NOTE: 1 ML  $HNO_3$   $\approx$  1%  $HNO_3$  BASED  
ON 1 ML 20% UNH SOLUTION  
SAMPLE

ML 0.154 N  $HNO_3$  / 50 ML

6 ML  $K_2Fe(CN)_6$

5 ML  $K_2Fe(CN)_6$

4 ML  $K_2Fe(CN)_6$

pH

860-8

END