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MONSANTO CHEMICAL COMPANY - UNIT III

DAYTON, OHIO

M. M. Haring
Laboratory Director

GAMMA SCALE CHEMISTRY PROGRESS REPORT

[redacted]
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Date: July 1-31, 1948

Prepared by: A. W. Martin

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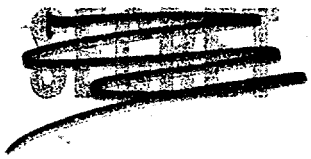

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GAMMA SCALE CHEMISTRY GROUP

B. Brody, M. Economides, E. Estabrook, E. F. Joy, and A. Martin

Oxide of Postum - A. Martin

A vacuum line is being rebuilt for use in an attempted preparation of the oxide of postum which may be formed by ignition of the residue formed when a solution of postum and nitric acid is carefully evaporated. Work on this problem was curtailed in July due to a vacation period and a visit to the Radiation Laboratory at Berkeley, California. There is no detailed report on the proposed preparation of the oxide of postum from a solution of nitric acid and postum. As soon as construction of the vacuum line and apparatus to be used in this preparation is finished experimental work will be undertaken.

Density of Postum - B. Brody

Calibration of a quartz capillary and filling a portion of this capillary with metallic postum, a repetition of the procedure reported in Ad Interim Report, MLM-103, Density of Metallic Postum by B. B. Brody, May 18, 1948, is underway. The experimental results are to be reported when all the necessary data have been obtained. No detailed report is included with the July 1-31, 1948, Gamma Scale Chemistry Progress Report.

Preparations - M. Economides

Abstract - Two phases of the experimental work on counting technique and subsequent counter calibration have been completed. These results will appear in an interim report.

Tellurium Compounds - E. Estabrook

Abstract - Analytical determination of the tellurium content of a sample of telluric acid crystals ($H_2TeO_4 \cdot 2H_2O$) was made. Using these data a standard solution of telluric acid was prepared for a potentiometric oxidation reduction titration against titanium trichloride as the reducing agent. Investigation of this oxidation reduction method is being made at the present time.

Bromides of Postum - E. F. Joy

Abstract - Investigation of the preparation and analysis of the bromides of postum is outlined indicating proposed methods of procedure.

Reaction of bromine and metallic postum has yielded two distinct crystalline forms or compounds of postum and bromine. From analogy to the preparation of the chlorides of postum these compounds formed with bromine and metallic postum are in all probability the di- and tetra-bromides of postum. Samples suitable for X-ray diffraction studies have been prepared and sent to the X-ray Group. It is indicated by the X-ray Group that the prepared bromide samples show patterns which are new and different from postum compounds previously studied.

An investigation of the potentiometric titration method on a micro scale of bromide ion with standard silver nitrate has been made. It is proposed to use this titration method as a quantitative measure of bromide ion present in the prepared samples of bromides of postum.

Preparations - M. Economides

Detailed Report - Experimental work on two phases of counting technique and calibration of the Simpson, Logac, and alpha counters has been completed. The results obtained in this completed work will appear in an interim report.

The first phase of this work consisted in checking Logac, Simpson, and alpha counters against calorimetric values. This was done by volatilizing metallic postum in a quartz tube, sealing off this tube and determining of the amount of activity present by calorimetry. This quartz tube was broken into a liter flask and 1.5 normal nitric acid added. Samples of this solution were prepared for Logac counting. Dilutions of this solution were prepared for Simpson and alpha counting. Results obtained are presented in the forthcoming interim report.

The second phase of the experimental work on counting technique consisted of checking Simpson and alpha counting against a series of calibrated pipets. A minimum of ten samples was prepared with each pipet. These results are treated statistically in the interim report.

A postum source as requested by Col. Naimark was prepared.

Future Plans - A request for 110 Logac and Simpson standards of postum and equilibrium materials has been received from the Electronics Section and will be prepared in the near future.

A series of blank determinations is being run on the calibrated pipets used in the work on counting technique. When these blank runs are completed the volumes of these same pipets will be determined using a microtitration method as a method of checking the mercury calibration.

Tellurium Compounds - E. Estabrook

Detailed Report - A solution of Mohler's stock telluric acid crystals ($H_2TeO_4 \cdot 2H_2O$) was prepared by dissolving crystals in double-distilled water. This solution was made to contain 1.9542 grams per liter. Quantitative analysis using sulfur dioxide gas as the reducing agent indicated a tellurium content of 54.30 per cent; theoretically, the tellurium content should have been 55.565 per cent. Standard solutions of approximately 0.1 normal titanium trichloride and of telluric acid have been prepared. Potentiometric titration using these standard solutions is under way; however, consistent results have not been experimentally obtained. Further investigation of the factors entering such an oxidation titration is in progress and will be continued.

Bromides of Postum - E. F. Joy

Detailed Report - Two crystalline compounds of postum were prepared by heating purified metallic postum in the presence of bromine vapor. These compounds appeared to be identical with those reported by A. W. Martin, Gamma Scale Chemistry Progress Report, May 1-31, 1948, MLM-123. In appearance the compounds formed with postum and bromine were dark red (black when in quantity) and yellow. The yellow crystalline form was separated from the red crystalline form in a capillary (22 micron wall, 0.5 mm. diameter, by volatilization at 250°C. The X-ray diffraction patterns of these two bromides obtained by R. E. Brocklehurst and L. F. Vassamillet indicated two new compounds of postum; however, there has been no interpretation of the X-ray diffraction patterns.

Investigation of the microtitration method for quantitatively determining bromide ion making use of standard silver nitrate in a potentiometric titration was made. A reference electrode of silver wire in 0.05 normal silver nitrate was used against an electrode

of silver in silver bromide. This titration which involves a precipitation reaction yields a titration curve which is dependent on the solubility product of the compound precipitated, in this case silver bromide. Comparison with a similar titration curve for chloride ion shows that the bromide ion gives a curve with a steeper slope and, therefore, it is possible to obtain a more precise end point with the bromide ion than with the chloride ion. Calculations for the titration concentrations used indicate that the addition of one per cent of the stochiometric amount of silver nitrate at the end point would show a potential drop of 127 millivolts. In the actual titrations, potential drops of 100 to 130 millivolts were observed and distinct end points were obtained. Typical titration curves for identical concentrations, 2 micromoles, of bromide ion and of chloride ion are shown in Figure 1. The steeper slope and sharper end point for the bromide ion is notable.

In order to check manipulative technique and the accuracy of a microtitration of bromide ion a standard potassium bromide solution was prepared. This standard potassium bromide was prepared from a weighed amount of reagent grade of a thoroughly dried, 170°C., sample of the salt. The normality of the silver nitrate solution used was checked gravimetrically on a macro scale from the weight of silver chloride precipitated from 50 ml. portions of the silver nitrate solution. All volumetric apparatus which was used was previously calibrated. Results of the micro titration of the potassium bromide against silver nitrate are given in Table I.

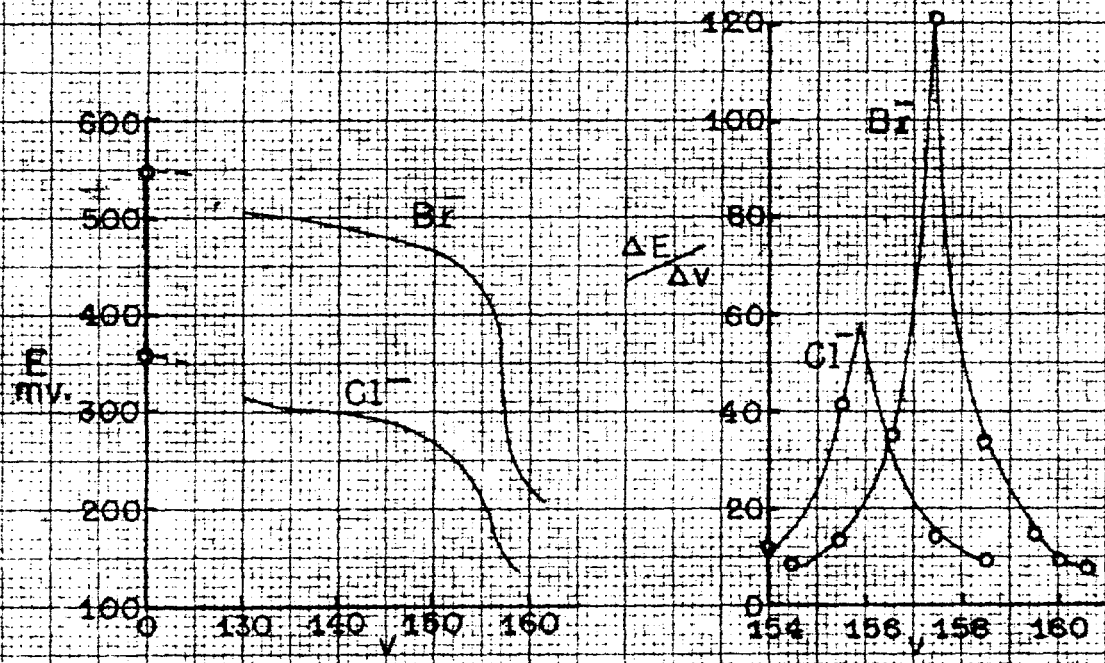
Table I

Standard KBr solution - 0.1006 N.

Standard $AgNO_3$ solution - 0.05007 N.

Microliters of KBr^-	Microliters of $AgNO_3$	Micromoles Br^- from Titration	Micromoles Br^- Taken
199.87	39.88	1.997	2.011
199.87	39.90	1.998	2.011
99.90	19.87	0.995	1.005
99.90	20.07	1.005	1.00[redacted]
99.90	20.07	1.005	1.00[redacted]

FIGURE 1



The quantities of bromide ion in the above titrations correspond to the bromide ion combining with 0.5 c. of postum, the larger value for postum tetrabromide and the smaller value for postum dibromide.

FUTURE PLANS

Of the various methods proposed in Gamma Scale Chemistry Progress Report, MLM-131, June 1-30, 1948, the direct reaction of metallic postum with bromine vapor contains fewer variables and thus is under consideration at the present time.

Outline of Problem

1. Preparation

a. Conditions, temperature and pressure.

b. Isolation tetra- from di- bromide.

c. Variation of bromine to postum ratio.

2. Physical and Chemical Properties of Both Tetra- and Di- bromides

a. Melting point.

b. Boiling point.

c. X-ray diffraction data.

d. Crystalline form.

e. Hydrolysis products.

3. Quantitative Determination of Formulas for Both the Tetra- and Di- bromides

a. Direct synthesis; postum by calorimetry. Bromine vapor by means of pressure measurements.

b. Potentiometric titration with silver nitrate, postum calorimetrically.

c. Quantitative weight measurements making [redacted] balance inclosed in vacuum. This proposed method will depend on the results of experiments now in progress within the Physics Group.