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MUM-237

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MOUND LABORATORY

Operated By

MONSANTO CHEMICAL COMPANY

MIAMISBURG, OHIO

M. M. Haring
Laboratory Director



# GAMMA SCALE CHEMISTRY PROGRESS REPORT



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Prepared by: A. W. Martin





 

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GAMMA SCALE CHEMISTRY GROUP

Group 4

M. Economides, E. Estabrook, E. F. Joy, A. W. Martin, and R. G. Yalman

| | Personnel | Man-Month - 1.0 | |
|---|---|---|---|
| General Problem | 202 | 204-C | 206-C |
| Determination of Formula, Methods of Preparation, and Properties of Compounds of Postum | 0.5 | | 0.5 |
| Specific Problems | | | |
| Bromides of Postum | | 1.0 | |
| Postum Compounds Formed in Solution | | 1.0 | 1.0 |
| Analysis of Impurities Accompanying Metallic Postum | 0.2 | | |
| Expediting Postum, etc. | | | 0.3 |
| Atomic Energy Show | 0.3 | | 0.2 |

ABSTRACT

The problem on the nature of the impurity which accompanies some of the samples of postum which was initiated in October, 1948[1] is being studied. An experimental study of the conditions necessary to produce the materials in an excited gaseous phase to be used for spectroscopic analyses is being made.

A projected experimental approach to new compounds of postum in particular those postum compounds which may be formed in solution has been initiated. The detailed report considers future plans with a statement of the work already begun.

Crystals of red postum bromide were prepared by treatment of a precipitate obtained from postum in aqueous ammonia with hydrobromic acid and upon removal of the liquid phase. This crystalline product was shown by comparison of X-ray diffraction patterns to be identical with the red postum bromide prepared by reacting postum metal and bromine vapor. A method for the separation of postum from associated anions was developed

[redacted]

which permits an analysis of these anions without interference from the alpha activity of postum. Over 99 per cent of the postum was removed from solution without appreciable loss of bromide ion. This procedure is based on the formation of a precipitate formed when the bromide of postum is treated with dilute ammonium hydroxide. This precipitate of postum and hydroxide was removed by filtration using a microcentrifugal filter, Figure 1. Two separate preparations of red postum bromide upon analysis using this method gave a bromide to postum ratio of 3.94 and 3.90 respectively, corresponding to a postum bromide formula of $QBr_4$.

DETAILED REPORT

Analysis of Impurities Accompanying Metallic Postum - A. W. Martin

The projected work[1] on an attempted analysis of what impurities accompany some samples of postum is being continued. Quartz spectroscopic tubes similar to those previously described, Figure 1,[1] have been constructed. A discussion with Donald Beaseeker suggested the need for an experimental investigation of the conditions necessary to obtain the materials used in these quartz tubes in an excited gaseous state. The pressures which may be used with the electrical source of excitation is being investigated. The Electronics Section is cooperating in supplying the needed excitation source. To date three excitation sources have been tried. The last source to be tried gives some promise of meeting requirements. As soon as this electrical source becomes available experiments will be run in order to determine optimum conditions for obtaining the materials under consideration in an excited gaseous state.

Postum Compounds Formed in Solution - E. Estabrook and R. G. Yalman

Two experimental procedures will be used to study the solution chemistry of postum. The first method will be to study the precipitation of postum with other elements and to determine whether or not true isomosphism occurs. Large crystals of host compounds will be prepared from postum containing solutions. Radiograms will be made of these crystals to determine whether postum is heterogeneously or homogeneously distributed or whether it is perferentially adsorbed on a particular growth plan (internal adsorption). At the same time postum will be co-precipitated with varying amounts of the host compound in order to determine whether it is carried in a logarithmic, linear or unrelated ratio. In this way it is hoped that the solid phase chemistry of postum can be studied and that the valence of postum as well as its coordination number will be determined under varying conditions.

Six normal hydrochloric acid and one and one-half normal nitric acid will be the first solvents used in this study. The experimental procedures will follow those described in Applied Radiochemistry by Hahn.[2]

[redacted]



The second procedure will be to study the exchange of postum on cation exchange resins. The theory and procedure to be used have been discussed by J. Schubert, Ion Exchangers.[3]

From this technique it is hoped that information will be obtained concerning the valence as well as the formation of postum complexes under varying conditions.

Work has been started on methods for preparing crystals of the following compounds:

$PbCl_2$

$(NH_4)_2\ PbCl_6$; $(NH_4)_2\ SnCl_6$; $K_2SnCl_6$

$ThCl_4 \cdot (?)H_2O$

$Mg_3Bi(NO_3)_6 \cdot 24H_2O$; $Mg_3Ce(NO_3)_6 \cdot 24H_2O$

Preparation of Postum Bromide from Hydrobromic Acid Solution - E. F. Joy

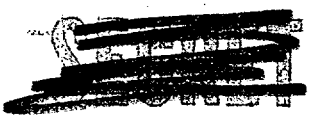
The precipitate of postum in ammonium hydroxide obtained from preparation B-4[1] and containing approximately 0.5 c. of postum was dissolved in fifteen lambda of forty per cent hydrogen bromide solution. The resulting orange-red solution was evaporated to dryness by passing a current of dry nitrogen over the solution at room temperature. Red crystals in appearance identical to the red postum bromide prepared by reacting bromine and metallic postum were obtained upon removal of the liquid phase. These red crystals were transferred into an X-ray capillary by distillation under a vacuum. An X-ray diffraction photograph of these red crystals taken by R. E. Brocklehurst showed the same pattern when compared with the pattern of postum bromide prepared from bromine and metallic postum.

Using the valence of plus four for postum in postum bromide the following cycle of reactions are indicated as taking place.

1. $Q + 2Br_2 \xrightarrow{\text{heat}} QBr_4$
2. $QBr_4 + xH_2O \longrightarrow QO_2 \cdot xH_2O \downarrow + 4HBr(aq)$
3. $QO_2 \cdot xH_2O + 4HBr(aq) \xrightarrow[\text{heat}]{\text{evaporate}} QBr_4 + xH_2O \uparrow$

$QBr_4$ is the product in both reactions (1) and (3).

[redacted]





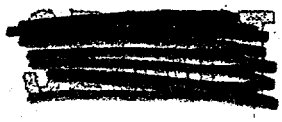
Preparation and Quantitative Analysis of Postum Bromide - E. F. Joy

Separation of postum from bromide ions in postum bromide using dilute aqueous ammonia was first tried in preparation B-3.[1] Removal of the bromide solution by means of a pipette was not entirely satisfactory due to the continuous stirring action of gas bubbles liberated in the solution. Washing of the precipitate containing fragments of the crushed Pyrex capillary in the centrifuge cone was difficult. Separation by filtration using microscale techniques led to the construction of the centrifugal filter shown in Figure 1.

Three preparations (B-5, B-6, and B-7) of red postum bromide were made by reacting postum metal with bromine. A microfilter was first used in the analysis of B-5, however, this sample had been prepared in a cone shaped reaction tube which made necessary an added transfer of solution and precipitate from the reaction tube to the filter. Preparations B-6 and B-7 were handled by the procedure given below.

The prepared postum bromide contained in a sealed thin walled capillary (1 mm. dia. ca. 10 mm. long) was calorimetered and the postum content determined. The capillary containing the postum bromide was placed in the microfilter covered with 100 lambda of 0.1 normal aqueous ammonia and then crushed by means of a small glass rod. Upon completion of precipitation by the aqueous ammonia the liquid phase was collected in the lower part of the centrifuge tube by centrifuging (about one minute). Rinsing of the glass rod used in crushing the capillary and five washings of the precipitate was made with twenty lambda portions of water.

The centrifuge tube, Figure 1, was scratched with a file at point A and the upper section cracked off using a hot glass rod on the file scratch to make the crack-off. The lower section containing the bromide solution served as a titration cell in a potentiometric micro-titration with 0.05 normal silver nitrate solution. Thirty lambda of 1.65 normal nitric acid was added. After titration of bromide ion content the solution was checked for postum content by calorimetry. Table I summarizes the quantitative analysis of prepared samples of red postum bromide.



# FIGURE 1

## MICRO CENTRIFUGAL FILTER

—SCALE: DOUBLE SIZE—

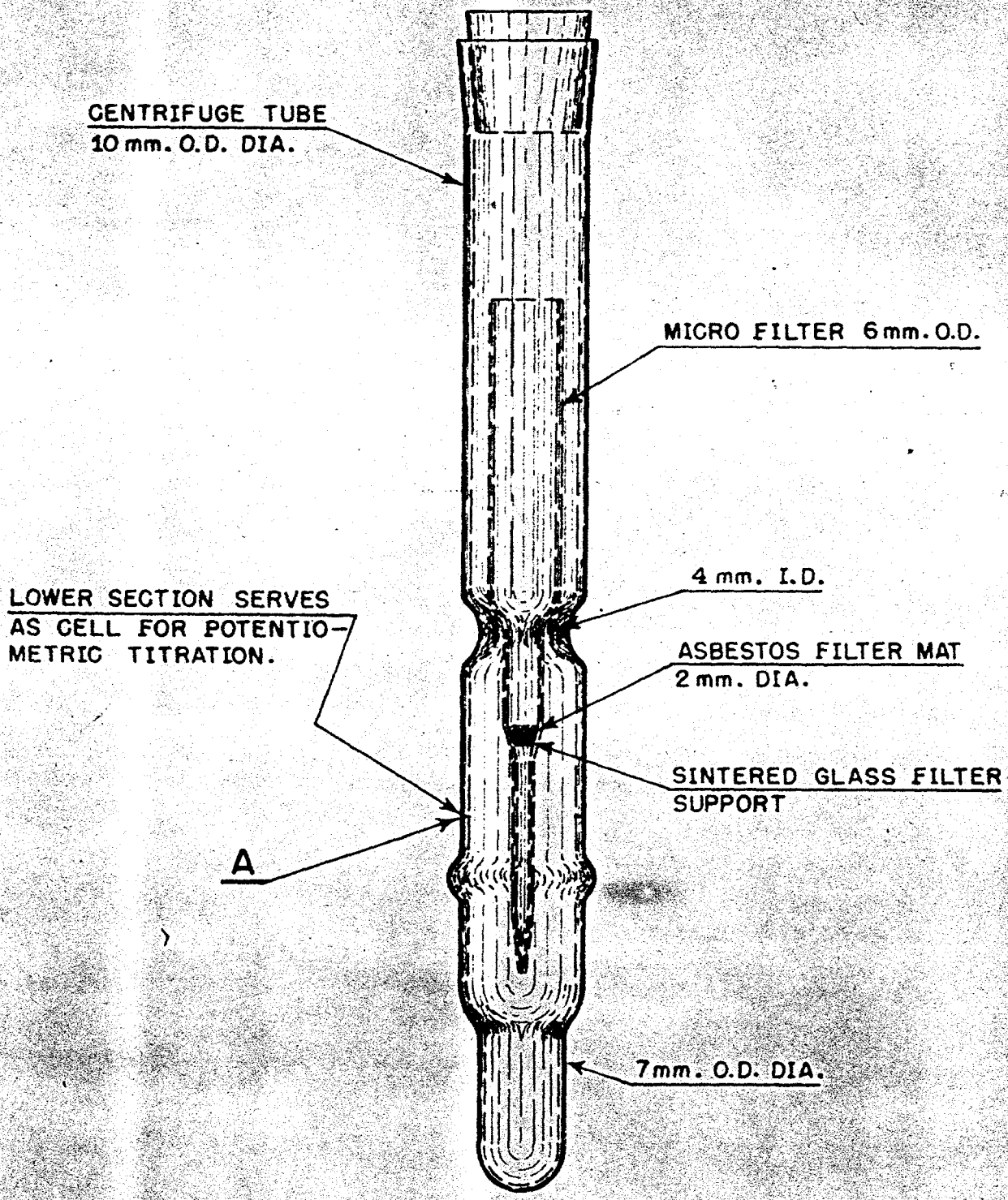


Table I

ANALYSIS OF RED POSTUM BROMIDE

| Sample Number | Postum Calorimetric Micromols | Bromide Ion Potentiometric Micromols | Ratio Br/Q | Postum in Titrated Solution C. | Postum Removed By Filtration Per Cent |
|---|---|---|---|---|---|
| B-5* | 0.257 | 0.858 | 3.35 | 0.015 | 93.8 |
| B-6 | 1.145 | 4.512 | 3.94 | 0.0008 | 99.9 |
| B-7 | 0.827 | 3.227 | 3.90 | 0.0069 | 99.1 |

*The value for Br/Q ratio in B-5 is probably low due to the extra solution transfer needed, also to the larger volume of the reaction tube into which bromine vapor could escape, both factors leading to a low bromide ion value.

Samples B-6 and B-7 give values of 3.94 and 3.90 for the bromide ion per postum atom ratio and within limits of experimental error show that the red postum bromide has a formula of $QBr_4$. This formula of $QBr_4$ is analogous to that of the higher chloride of postum, $QCl_4$, already established.[4,5] The data in Table I also shows that for the procedure used over 99 per cent of the postum is removed by precipitation with aqueous ammonia from the postum bromide in solution.

Additional analyses of preparations of the red postum bromide are planned in order to confirm the bromide ion postum ratio which has been obtained. In addition, it is planned to repeat the titration of free acid formed in the hydrolysis reaction of the red bromide, modifying the method to a back titration procedure, adding a known amount of hydroxide, filtering out the precipitated postum and then titration of excess hydroxide with standard acid.

REFERENCES CITED

1. A. W. Martin, Gamma Scale Chemistry Progress Report, MLM-215, October 1-31, 1948.

2. Otto Hahn, Applied Radiochemistry, Cornell University Press, 1936.

3. J. Schubert, Ion Exchangers, Clinton Laboratory, CNG-3380.

4. E. F. Joy, Information Meeting Paper No. 5.

5. E. F. Joy, Fundamental Chemistry Progress Report, November 16-30, 1947.

AWM/rcc