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GALIA SCALE CHEMISTRY PROGRESS REPORT

Restricted Data

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Prepared by: A. W. Martin

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General Problem

Determination of Formula, Methods of Preparation, and Properties of as Many Compounds of Postum as Possible

Specific Problems

Oxide of Postum

X-ray Capillary of Metal

Examination Quartz-Fibers

Analysis Incurities Occurring with Metallic Postum

Source Preparations

Bromides of Postum

Tellurium Compounds

Expediting Postum, etc.

Personnel

Man - Month = 1.0

202-C, 204-C, 206-C

0.2

0.5

0.1

0.1

0.1

0.8

1.0

1.0

0.2

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GARKA SCALE CHEMISTRY GROUP

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* Terminated September 3, 1948.

ABSTRACT

Oxide of Postum - A. Martin

Postum dioxide, CO₂₅, can be prepared from a solution of postum in nitric acid. In recently completed experiments postum dioxide was prepared by heating at approximately 273°C, a residue obtained from a nitric acid solution of postum. Metallic postum purified by fractional volatilization as well as reduction with dry, oxygen free hydrogen was reacted with concentrated nitric acid. The liquid phase from this nitric acid solution of postum was removed by distillation under reduced pressure. A resulting white residue formed in this distillation procedure was loosened and shaken into an X-ray capillary. A yellow residue similar in appearance to postum dioxide was obtained on heating this white residue under reduced pressure at approximately 273°C. An X-ray diffraction powder pattern of this resulting yellow crystalline residue yielded an X-ray powder pattern identical to that previously obtained for postum dioxide, CO₂₅.₃ These experiments, i.e., preparation of postum dioxide from a solution of postum in nitric acid, are considered as completed.

Preparation of an X-ray Sample of Pure Metallic Postum - A. Martin

Starting with a sample of previously purified, metallic postum, approximately 1 l. c. of this sample was subjected to volatilization procedures. A final volatilization step was used to collect the crystalline metal sample in a Pyrex X-ray capillary suitable for X-ray diffraction powder photographs. This prepared sample in an X-ray capillary was turned over to R. E. Brocklehurst and the X-ray Group. No detailed report is included in this progress report.

Examination of Used Quartz-Fibers - A. Martin

Work has been completed on the microscopic examination of the quartz-fibers from the quartz-fiber balance which had been in use for some time by the Microassay Group. The data and photomicrographs together
with a report discussing these data have been turned over to R. G. Olt. No detailed report is included in this progress report.

Separation and Analysis of Impurities Occurring with Metallic Postum Samples - A. Martin

Experiments are to be undertaken in an attempt to determine what impurities are present with the postum when the metallic postum is deposited on platinum foils or gauges with special emphasis on that fraction which is condensed out below 250°C. when using a volatilization procedure.1 These experiments are being formulated and it is proposed to make use of spectroscopic analysis.

Preparations - M. Economides

The Simpson standards for the counting room have been completed. All but four of forty Logac standards have been prepared and delivered to the counting room.

Tellurium Compounds - E. Estabrook

Solutions of varying concentrations of nitric acid with an excess of tellurium have been prepared. Aliquots of these tellurium solutions have been titrated against standard titanium trichloride. The results are discordant. This work with tellurium will be temporarily discontinued in order to avoid an overdose of the toxic tellurium.

Bromides of Postum - E. F. Joy

A ratio of 2.5 atoms of bromide ion per atom of postum was obtained for one sample of red postum bromide crystals; however, the appearance of bromine vapor in the tube containing the postum bromide crystals indicates decomposition. The analytical method used to establish this bromide ion to postum ratio was a potentiometric titration with silver nitrate. Although a satisfactory end point was obtained this potentiometric titration does not titrate free bromine. A modified method of analysis which would account for free bromine as well as bromide ion is proposed.

Two X-ray capillaries containing samples of ThBr₄ and ThOBr respectively, were prepared. The X-ray diffraction pattern from the ThBr₄ was not satisfactory. The sample of ThOBr₂ gave an X-ray diffraction pattern
which indicated an amorphous rather than a crystalline material.

DETAILED REPORT

Oxide of Postum  -  A. Martin

About 1.2 c. of purified metallic postum was contained in a small quartz capillary was broken open and inserted in a capillary cone. Twenty lambda of concentrated nitric acid was added to the capillary cone containing the metallic postum. The resulting solution of postum in nitric acid was transferred by means of a capillary pipet to a Pyrex reaction tube, Figure 1. This reaction tube, containing the nitric acid solution in the bend as indicated in Figure 1, was connected to a liquid air trap which in turn was attached to the vacuum system. Partial reduction (100 mm. of mercury) from atmospheric pressure removed the liquid phase of the solution of postum in nitric acid. A white residue remained after removal of the liquid phase.

This white residue was loosened from the reaction tube and shaken into the small (20 micron wall 0.3 mm. diameter) capillary end of the reaction tube, Figure 1. It was necessary in this procedure of transferring the residue to the capillary end to bring the reaction tube to atmospheric pressure, open to the atmosphere and to insert a Pyrex glass rod.

After transfer of the white nitrate residue to the capillary end, the reaction tube was replaced on the vacuum system and thoroughly evacuated, 1 x 10^-4 mm. of mercury. A tubular electrical heated furnace was placed around the active deposit in the capillary end. The temperature inside this furnace was maintained between 275°C. and 281°C. for five hours. A yellow crystalline active material was obtained in the capillary end. In appearance this yellow residue was identical to that prepared when dry oxygen gas was reacted with metallic postum.

This capillary tube was sealed off and mounted in an X-ray capillary holder. This sample of yellow oxide in the X-ray capillary was given to R. E. Brocklehurst of the X-ray Group. A report from that group confirms the preparation of postum dioxide, O₂, when the nitrate residue of postum is heated.
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FIGURE 1

PYREX REACTION TUBE FOR PREPARATION OF POSTUM DIOXIDE FROM A SOLUTION OF POSTUM IN NITRIC ACID

SCALE: FULL SIZE

18/9 BALL JOINT

TO COLD TRAP AND VACUUM SYSTEM

10 MM. O. D. PYREX

POSTUM IN NITRIC ACID

SCALE: FULL SIZE

X-RAY CAPILLARY

20 MICRON, WALL

0.30 MM. O. D.
The experiment as reported above gives another means for the preparation of postum dioxides. The first successful quantitative preparation of CO₂ by direct union of postum and oxygen and proof of an oxidation state of plus four was further confirmed from X-ray capillaries of this yellow oxide prepared by oxidation of metallic postum. These X-ray capillaries prepared by direct union of postum and oxygen have been shown by X-ray analysis to be postum dioxide. Further proof that the yellow oxide X-ray diffraction pattern is that of CO₂ is shown in the almost identical X-ray diffraction pattern for thorium oxide. It may be concluded from these experiments that the residue from a solution of postum in nitric acid when heated at 278°C, under reduced pressure is converted to postum dioxide, CO₂.

Separation and Analysis of Impurities Occurring with Metallic Postum - A. Martin

It has been found necessary for the preparation of compounds of postum to use a lengthy, stepwise procedure for the purification of metallic postum before undertaking preparation of these compounds. The steps in the purification procedure have been previously described and are essentially fractional volatilization steps of the postum from the platinum foils or gauze on which it is received. These volatilization steps are carried out under reduced pressure. It has been observed in the volatilization step at 200°C, also below this temperature, that frequently a noticeable amount of dull brownish black material deposits in the cooler portion of the volatilization tube. This material volatilizing at and below 200°C, does not fluoresce to any extent and contains a very small fraction of the metallic postum which is present in the tube.

Experiments are being undertaken in an attempt to determine what impurities are present with metallic postum when deposited on platinum with special emphasis on that fraction which is condensed out at or below 200°C. When using a volatilization procedure. It is proposed to make use of spectroscopic analysis of four materials in as many specially prepared quartz tubes. The materials are to be contained under a pressure of 1 x 10⁻⁵ mm. of mercury in each of four tubes. As a suggested first analysis the following materials will be used:

1. Pure mercury.
2. Pure lead.
3. Purified metallic postum.
4. Material volatilizing at or below 200°C. obtained in the volatilization step of postum.

Work on the construction of the necessary quartz tubes and connecting apparatus is under way.

Preparations - M. Economides

All of the Simpson standards prepared from equilibrium solution have been delivered to the counting room. There were seventy standards ranging from 2000 to 200,000 c./min.

Thirty-six Logac standards prepared from postum solutions were made and delivered to the counting room. These ranged from $1 \times 10^8$ to $1 \times 10^9$ d./min.

Future Plans - An investigation of counting technique will continue. Calibrations of the micropipets which were used in this investigation are being checked for delivered volume. A potentiometric method using silver nitrate and potassium bromide as primary standards is being tried.

Bromides of Postum - E. F. Joy

Analysis of postum bromide preparation No. B-2. This sample containing 0.170 micromoles of postum was dissolved in 200 lambda of 0.2 normal nitric acid. The resulting solution was titrated with 0.05 normal silver nitrate for bromide ion content using the procedure previously described. A satisfactory endpoint was obtained. Results of analysis on this sample of postum bromide gave a value of 0.415 micromoles of bromide ion per 0.170 micromoles of postum or a bromide ion to postum ratio of 2.44 to one. The appearance of free bromine was observed in the sealed tube containing the sample of postum bromide. The potentiometric method using silver nitrate accounts for the bromide ion but not for any free bromine which may have resulted from the decomposition of the postum bromide. A procedure is being developed to account for both free bromine and bromide ion. It is proposed to take up the postum bromide with a solution of ammonia, neutralize the excess hydroxide with nitric acid and then titrate with a standard silver nitrate solution.
Thorium Bromide and Thorium Oxybromide — Thorium bromides prepared by reacting thorium oxide, sugar, carbon, and bromine was collected in a quartz X-ray capillary. The X-ray pattern as obtained by the X-ray Group indicates presence of material other than crystalline thorium bromides. Thorium oxybromide prepared by hydrolyzing thorium bromide and drying at 160°C, was shaken into an X-ray capillary. The X-ray diffraction pattern of this sample of oxybromide showed the presence of a few faint lines indicating this sample was amorphous and not crystalline.

REFERENCES CITED


