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DETERMINATION OF ORGANIC MATERIAL IN AQUEOUS SOLUTIONS

by

E. R. Russell
Analytical Chemistry Division

August 1954

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CHEMISTRY - SEPARATION PROCESSES
FOR PLUTONIUM AND URANIUM

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CHEMISTRY - SEPARATION PROCESSES
FOR PLUTONIUM AND URANIUM

ABSTRACT

A method was developed for determining the concentration of trace quantities of organic material in aqueous solutions. The organic material is oxidized in solution, followed by gasometric measurement of the carbon dioxide. The technique may be applied to radioactive solutions, and as little as 0.3 of a micromole of carbon can be determined.

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DETERMINATION OF ORGANIC MATERIAL IN AQUEOUS SOLUTIONS

INTRODUCTION

In the separation of metallic ions by extraction processes traces of the organic extractant remain in the aqueous phase. It is desirable to determine the organic content of the aqueous phase and to make the method applicable to radioactive solutions.

Analytical methods described in the literature are not suitable for this problem, for various reasons. Some are not fast enough for routine use, some are fast but not accurate, and most require samples that are too large for work with highly radioactive solutions.

A combination of existing techniques offered promise of meeting the objectives of this study. The classical method for carbon determination via oxidation to carbon dioxide, combined with modern techniques for collecting and measuring small quantities of this gas, was selected as a basis for experimental work.

SUMMARY AND CONCLUSIONS

Wet oxidation and gasometric measurement of evolved carbon dioxide were used to determine various organic compounds in aqueous solutions. Samples containing known quantities of organic material were analyzed with average recoveries ranging from 93.8 to 102.5 per cent. The precision for a single determination, expressed as standard deviation, was ± 2.7 per cent.

The volume of the gas-measuring system defines the sensitivity and range of the method. A gas-measuring volume of one milliliter is satisfactory for measuring about three tenths to about twenty-five micromoles of carbon dioxide.

Although this study was limited to the determination of relatively nonvolatile organic compounds such as tri-n-butyl phosphate, the method should be applicable to more volatile substances since the gases leaving the wet-oxidation chamber are subject to further oxidation in the combustion furnace.

The method is being used for analysis of special samples in the laboratory and is satisfactory for routine plant use.

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DISCUSSION

BACKGROUND

The problem of determining small amounts of hydrocarbons in water has long confronted the oil industry, where pollution of streams is of paramount importance. In order to assist petroleum refiners in their efforts to remove oil from refinery effluent waters, a group of laboratories working cooperatively through the American Petroleum Institute's Committee on Analytical Research (1) has developed or evaluated six new methods for determining oil in water. The infrared method (2) was reliable for oil concentrations as low as 0.1 ppm with an accuracy of ± 20%, but the method was unsatisfactory for routine use. Other methods were also investigated, such as extraction of the oil with various solvents followed by separation of the oil from the solvent and/or by density analysis of the oil-in-solvent solution. The results of the analyses on the various standard samples submitted to the different laboratories varied from 85 to 160% of the true values. Each laboratory made use of one of the previously evaluated methods. The size of samples required for analysis prohibits the use of any of the above methods for radioactive solutions.

The classical methods for the determination of carbon in organic compounds involve conversion to carbon dioxide and collection of the gas either by chemical absorption or by condensation. Templeton and Watters (3) have discussed the advantages of both methods.

Smiley (4) described a method developed for determining traces of carbon in a metal. In this method the carbon was oxidized in a stream of oxygen passed over the heated metal. The carbon dioxide was condensed in a capillary trap cooled with liquid nitrogen and its pressure and volume were then measured at room temperature. The main advantage was that high-vacuum techniques were not required as in conventional condensation methods. This method appears to be limited only by the volume of the gas-measuring system and the accuracy of determining the pressure.

Mayer, Ader, and Ross (5) employed a wet oxidation combined with a conductometric measurement for the determination of organics in aqueous systems. The organic matter contained in the aqueous solution was oxidized to carbon dioxide with a mixture of chromic acid, sulfuric acid, phosphoric acid, and potassium iodate. The evolved carbon dioxide was swept through the system with oxygen and was absorbed in a 0.01N sodium

[redacted]

hydroxide solution. The change in conductivity of the alkaline solution was a linear function of the carbon content of the sample up to 1.5 mg. The sensitivity of the method was given as 0.1 mg ± 0.02 mg. of carbon.

OUTLINE OF METHOD

In the method reported here, a controlled stream of oxygen is purified and admitted to a wet-combustion chamber where organic material in the sample is oxidized to carbon dioxide. The resultant gases are swept from the chamber by the oxygen carrier and are passed over hot copper oxide to insure complete combustion. The gases are then purified prior to admission to the gas-measuring system where carbon dioxide is condensed in the capillary trap by liquid nitrogen. The trap is evacuated at the end of a run, and then is warmed to room temperature and the amount of carbon dioxide is measured.

From a preliminary analysis, an estimate of the optimum sample volume may be made, the optimum quantity of carbon dioxide is determined by the volume of the gas-measuring system. For this work, the sample volume was consistently below 1 ml.

APPARATUS

The essential parts of the apparatus as shown on page 10 are as follows:

Symbol	Description
Oxygen Purification	
G	Four liter aspirator bottles for maintaining a constant oxygen pressure.
T_1	Drying tube filled with silica gel for drying the oxygen
O_1	Microcombustion tube filled with copper oxide
F_1	Furnace for heating the combustion tube, maintained at 600°C.
T_2	Absorption tower filled with Ascarite covered with a layer of silica gel
Oxidation	
C	Trap and gas inlet tube

V	Reaction vessel, with side arm for addition of oxidant
T_3	Air-cooled trap
O	Auxiliary combustion tube filled with copper oxide in the heated portion, and with powdered silver and copper in the unheated portion ((outlet end)
F_2	Furnace maintained at 600°C

Gas Purification

T_4	Absorption tower filled with "Anhydrone" for removing water from the carbon dioxide
T_5	Trap cooled by dry ice for the removal of condensable nitrogen oxides

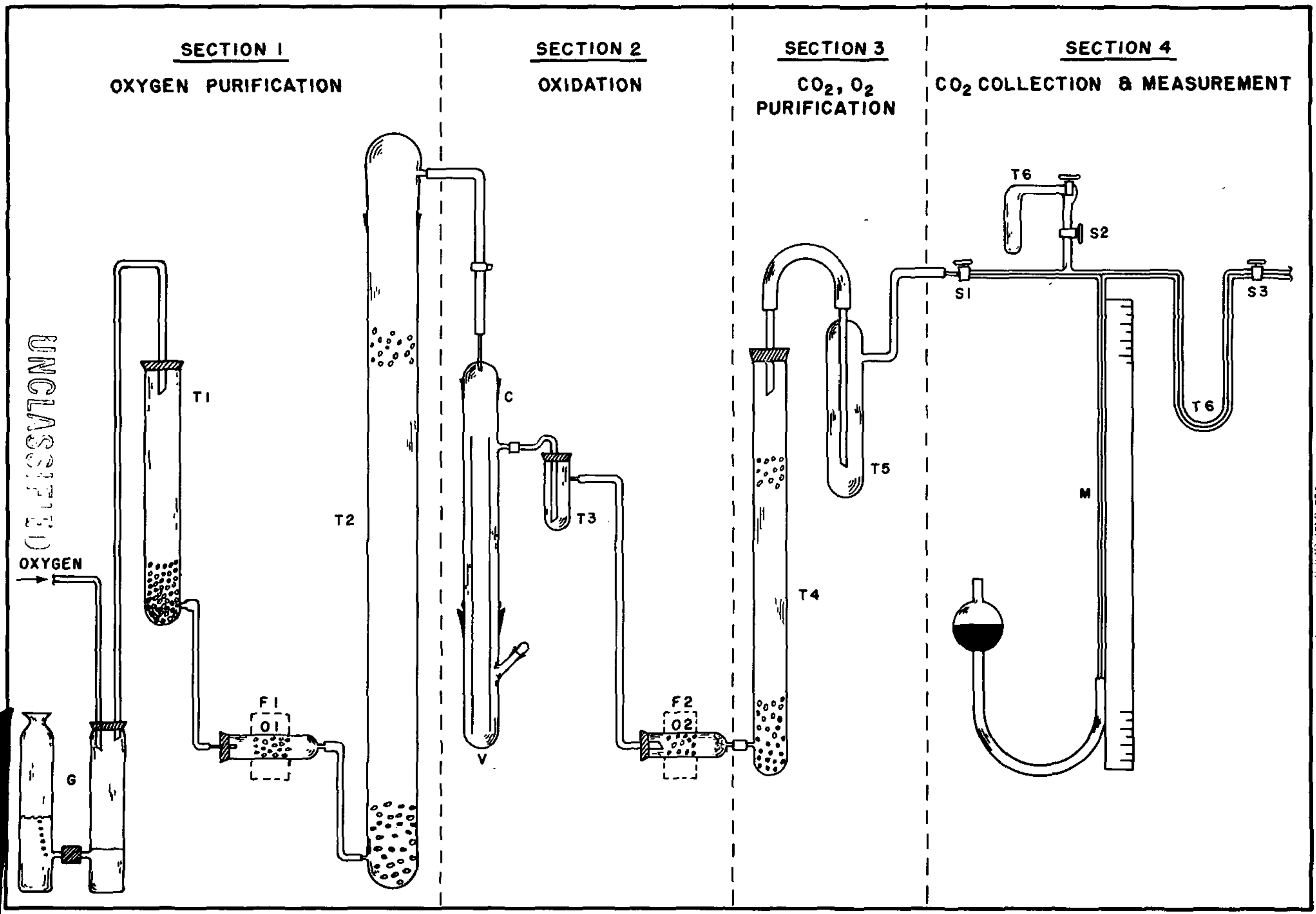
Carbon Dioxide Collection and Measurement

S_1, S_2, S_3	Stopcocks
T_6	Side trap for collecting samples for mass spectrometric analysis
T_7	Measuring trap cooled in liquid nitrogen
M	Capillary manometer

The wet-oxidation chamber consists of a modified trap, C_1, connected to the reaction vessel, V , by a ground joint. Oxygen enters the chamber through the inner tube of C_1, which extends almost to the bottom of the reaction vessel so that the solution is thoroughly oxygenated.

The auxiliary combustion train contains a microcombustion tube filled at the unheated end with powdered silver and copper. The heated portion is filled with copper oxide. Here any partially-oxidized carbon is converted to carbon dioxide and chlorides are removed if present.

The gas collection and measurement portion of the apparatus is very similar to that used by Smiley (4) with the addition of the side trap, T_6, for collecting samples for mass spectrometric analysis. Stopcock, S_1, is used for admitting the gas



CARBON DETERMINING APPARATUS

sample into the measuring system and S_3 is connected to the vacuum pump. Stopcock, S_2, is used for transferring a gas sample to a sample tube. The "U" trap, T_7, is made of 1.5 mm capillary tubing; during the period that CO_2 is evolved, it is cooled with liquid nitrogen. The capillary manometer (2 mm capillary tubing) has a zero mark about four cm below the T joint. The volume included between this mark and stopcocks S_1, S_2, and S_3 is determined. To this must be added the volume contribution of the manometer change which in this apparatus was 0.031 ml per cm.

PROCEDURE

Determination of the Blank Close stopcocks S_1 and S_2 and open S_3. Evacuate the gas-measuring system and adjust the mercury level in the manometer to the zero mark. Open stopcock S_1 slowly and pass oxygen through the system at about 40 ml per minute. The mercury in the manometer should fall about 5 cm for this flow rate. The flow rate is not critical, but should be the same for both sample and blank. Continue the flow of oxygen through the system for about 30 minutes and then cool the "U" trap with liquid nitrogen for 25 minutes. Close stopcock S_1 and continue evacuation until the mercury in the manometer rises to the zero mark. About $1\frac{1}{2}$ minutes is sufficient for removal of all non-condensable gases. Close stopcock S_3 and remove the cooling liquid from the "U" trap. Allow the system to warm to room temperature and record the mercury level in the manometer.

Calculate the moles of gas using the ideal gas law. If the blank is greater than 0.2 micromole, the operation should be repeated. Unless the apparatus has been open to the atmosphere for long periods of time only one flushing with oxygen is necessary. The above procedure is repeated with the reagents added and the reaction vessel and combustion furnace heated. The reagents are acceptable if they do not measurably increase the blank.

Analysis of Samples While the combustion furnace is warming to the desired temperature, remove the reaction vessel and add to it 1 ml of water. A known volume of sample is added below the surface of this water to prevent creepage of surface-active organic substances. Return the vessel to the system and close off the oxygen supply with a pinch clamp on the tubing connection above the reaction vessel. Remove the glass plug from the side arm of the reaction vessel and add 7 ml of oxidant (10 M sulfuric acid saturated with potassium dichromate) to which has been added a volume of concentrated sulfuric acid equal to the volume of water plus sample already in the reaction vessel. Cool the "U" trap with liquid nitrogen after removal of all gas from the gas-measuring system. Restopper the reaction vessel, remove the pinch clamp, heat the reaction vessel and while stopcock S_3 is open, slowly open stopcock S_1 until the pressure in the manometer reads the same as in the blank determination. Continue to pass oxygen through the system for 25 minutes while the reaction mixture is maintained just below its boiling temperature.

Close stopcock S_1 and evacuate the gas-measuring system for $1\frac{1}{2}$ minutes and close stopcock S_3. Remove the liquid nitrogen from the "U" trap and allow the system to warm to room temperature. Record the mercury level in the manometer.

A typical analysis for tri-n-butyl phosphate (TBP) is recorded and calculated as follows:

Volume of sample.	0.5 ml
Zero level of mercury in manometer.	83.4 cm
Recorded level of mercury after run	73.4 cm
Pressure of gas	10.0 cm
Calibrated volume of system	1.03 ml
Volume increase = 10.0 cm x .031 ml/cm.	0.31 ml
Volume of collected gas	1.34 ml
Room temperature = ...	27°C

$$N_{\text{Moles of gas}} = \frac{10.0 \text{ cm} \times 1.34 \text{ ml}}{76 \text{ cm} \times 82.06 \text{ ml-atm/(degree mole)} \times 300^\circ}$$

$$= 7.17 \times 10^{-6} \text{ moles}$$

$$N_{\text{gas}} - N_{\text{blank}} = N_{CO_2}$$

$$7.17 \times 10^{-6} \text{ moles} - 0.2 \times 10^{-6} \text{ moles} = 6.97 \times 10^{-6} \text{ moles } CO_2$$

$$6.97 \times 10^{-6} \text{ moles } CO_2/12 = 5.8 \times 10^{-7} \text{ moles TBP}$$

$$\text{Grams TBP/ml} = 266 \text{ g/mole} \times 5.8 \times 10^{-7} \text{ moles} \div 0.5 \text{ ml}$$

$$= 3.08 \times 10^{-4} \text{ g/ml} = .031 \text{ weight } \%$$

In this study blank determinations were made before each series of runs and after three or four determinations.

RESULTS

The following table shows blank determinations including runs in which nitric acid was added as a sample:

BLANK DETERMINATIONS

Sample, ml	Oxidant, ml	Oxygen, ml	Nitrate, molarity	Blank, micromoles of carbon
2	7	1000	0.8	0.2
0	10	1000	-	0.2
0	-	1000	-	0.2
0	10	2000	-	0.4

To test the efficiency of the apparatus, a standard potassium acid phthalate solution containing 3.85 micromoles of carbon per ml was analyzed. Potassium acid phthalate is easily oxidized by sulfuric acid-dichromate solutions; in this case a 15-minute oxidation time suffices. However, in order to standardize the procedure and make it applicable to substances more difficult to oxidize, a 25-minute oxidation time was used. The results are shown in the following table:

ANALYSIS OF POTASSIUM ACID PHTHALATE SOLUTIONS

Volume of Sample, ml	Nitrate, Molarity	Carbon Present, Micromoles	Carbon Found, Micromoles	Std. Dev. Micromoles
0.20	0.2	7.6	7.8	-
0.25	-	9.6	9.3	± 0.26[a]
0.50	-	19.3	18.0	-

a = 8 determinations

As a further test of the oxidation efficiency, saturated aqueous solutions of tri-n-butyl phosphate were analyzed. The solutions were prepared by equilibrating carefully purified TBP with distilled water (Appendix B). The first mixture was agitated for 8 hours and the phases were allowed to separate by standing 16 hours; the second was treated in the same manner for 16 and 48 hours. The data in the following table show that saturation was complete and that the phases were completely separated. The value of 0.051 ± 0.002% for the solubility of TBP in water is slightly higher than results previously reported (6). This fact indicates that oxidation was complete in every case.

THE DETERMINATION OF TBP IN AQUEOUS SOLUTION

	Sample Volume, ml	TBP micromoles	weight % TBP in H_2O	
Solution 1	0.50	0.96	0.051	0.003[a]
Solution 2	0.50	0.97	0.052	0.003[b]

a = 5 determinations
b = 7 determinations

Similar analyses of aqueous solutions of kerosene indicated that oxidation was complete.

Samples of carbon dioxide obtained from the oxidation of potassium acid phthalate and from the TBP solutions were analyzed for impurities by mass spectrometry. The impurities contributed less than 2 per cent to the total volume of the gas.

E. R. Russell
E. R. Russell
Analytical Chemistry Division

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APPENDIX A

CHEMICALS AND REAGENTS

Commercial oxygen was purified by passing it through a drying tower filled with silica gel, through a microcombustion tube filled with copper oxide maintained at a temperature above 750°C, and then through a tower containing Ascarite covered with a layer of silica gel.

The standard test solution contained 0.0262 gram potassium acid phthalate in 200 ml of distilled water. This is equivalent to 3.85 micromoles of carbon per ml.

The tributyl phosphate was synthesized and was free of hydrolysis products. All other chemicals used were of ACS reagent grade.

APPENDIX B

SATURATION OF WATER WITH TRI-n-BUTYL PHOSPHATE

A dropping funnel with its stem bent upward to extend above the level of water in a water bath was closed at the stopcock. Equal volumes of TBP and distilled water were added to the funnel and the funnel was partially immersed in the water bath maintained at 26°C. The mixture was stirred mechanically for eight hours and the stirrer was then removed. The solution was allowed to stand undisturbed for sixteen hours for complete separation of phases. The stopcock was opened and the aqueous phase was allowed to fill the side arm of the funnel. The top portion of liquid in the side arm was drawn off and discarded. Aliquots of the aqueous solution were then taken and analyzed. The procedure was repeated with sixteen hours' stirring and forty-eight hours' standing.