Absorbents in Microanalysis. III*. Lead Chromate as an External Absorbent in the Microanalysis of Chlorine, Bromine, and Sulphur

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A simple method for microdetermination of chlorine and bromine is described. Halogens are absorbed by lead chromate at about 400⁰, and determined from the increase of weight of lead chromate. It was found that at 400⁰ microquantities of halogens catalyse quantitatively the oxidation of sulphur dioxide to sulphur trioxide; thus from the combined weight of the halogen and sulphur trioxide the percentage of sulphur and halogen can be calculated.

Lead chromate has been used in classical microanalysis of carbon and hydrogen as an oxidant as well as an absorbent for halogens and sulphur[1,2]. Some years ago its use as the external absorbent in microanalytical gravimetric determination of sulphur was claimed[3]. Recently an absorbent for absorption of fluorine prepared from lead carbonate and silver carbonate was also described[4]. In this paper the use of lead chromate as the external absorbent in microanalytical determination of chlorine and bromine is described.

EXPERIMENTAL

Apparatus

The apparatus, except the absorption train and the filling of the combustion tube, is the same as the one described earlier[5]. The absorption train (Fig. 1.) consists
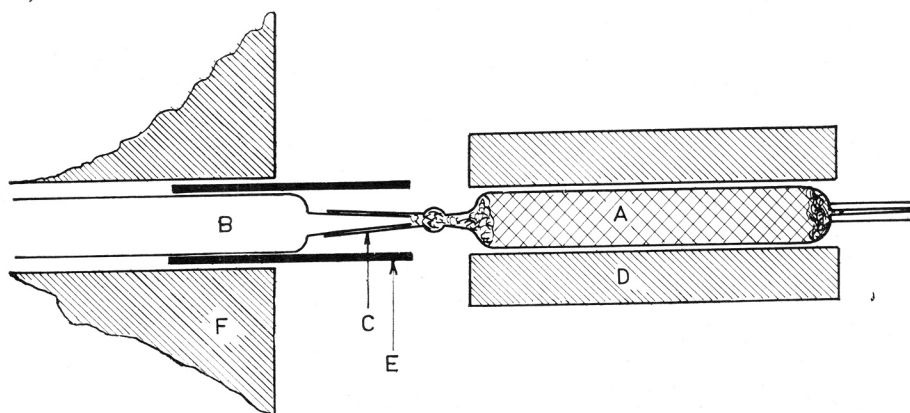

Fig. 1. Absorption train for the determination of halogens and sulphur by lead chromate. A-Halogen and sulphur absorption tube; B-Combustion tube; C-Ground glass joint; D-Furnace; E-Metallic cylinder (4.5 × 1.5 cm.); F-Furnace.

* Part II.: O. H a d ž i j a, *Mikrochim. Acta* (Wien), in press

of an absorption tube A (7×1 cm.) and a furnace D which is heated to 380—400⁰.
A is filled with layers of: 0.5 cm. quartz wool, 6.0 cm. lead chromate (B. D. H. Micro-
analytical Reagent), and 0.5 cm. quartz wool. One end of A is connected to the
combustion tube B with ground glass joint C (Quickfitt B5), and the other is a
capillary tube. C is warmed by the metallic cylinder E — 2 cm. of which extend
into the furnace F. The furnace F is heated to 800—850⁰. The combustion tube is filled
only with quartz wool.

Procedure

The absorption tube is attached to the preheated combustion tube and oxygen
in passed through the system for 40 min. at a rate of 15 ml/min. It is removed, cooled
for 15 min. near the balance, weighed and then replaced in the combustion train.
A weighed sample, estimated to contain 0.5—2.0 mg. of chlorine or bromine, is
introduced, oxygen flow is resumed, and the sample is burned carefully over a period
of about 20 min. Sweeping with oxygen is continued for another 20 min., the
absorption tube removed, cooled for 15 min. and weighed. Halogen is determined
directly from the increase in weight of the absorption tube. In the absence of halogens
sulphur may be determined in a similar manner by weighing sulphur trioxide
absorbed on lead chromate that has been pre-treated with halogen.

RESULTS AND DISCUSSION

Fourteen halogen-containing compounds were tested (Tables I and II). The
absorption of chlorine and bromine was quantitative at 400⁰; iodine was not
absorbed by lead chromate at this temperature. Nitrogen did not interfere with
the determination. The saturation of lead chromate is evident from the change
of colour from brick-red to green-yellow.

TABLE I

*Gravimetric Microdetermination of Chlorine and Bromine by Absorption
on Lead Chromate*

Compound	% Cl			% Br		
	Calc'd.	Found	Error	Calc'd.	Found	Error
4-Chlorobenzoic acid	22.65	22.53	— 0.12			
2.4,5-Trichlorophenol	53.86	54.29	+ 0.47			
4-Chloro-2,3-dinitrobenzene	17.50	17.37	— 0.13			
4-Bromobenzoic acid				39.75	39.92	+ 0.17
2-Bromoethylamine $\times$ HBr				83.71	83.46	— 0.25
N-Bromosuccinimide				44.90	44.99	+ 0.09
(3,4-Dimethyl)-phenyl-hydrazine $\times$ HCl	20.54	20.14	— 0.40			
(2-Methoxy)-phenylhydra-zine $\times$ HCl	20.30	19.88	— 0.42			
5-Benzyloxy-3-(N-morpholyno-ethyl -indole $\times$ HCl	9.51	9.83	+ 0.32			
5-Benzyloxy-3-(N-piperidino-ethyl)-indole $\times$ HCl	9.56	9.78	+ 0.22			
5-Benzyloxy-3-(N-pyrrolidino-ethyl)-indole $\times$ HCl	9.94	9.43	— 0.51			
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl chloride	9.70	9.23	— 0.47			
2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide				19.43	19.09	— 0.34
Dibenzyl L-glutamate $\times$ HCl	9.75	9.80	+ 0.05			

TABLE II

Mean Error of Results of Chlorine and Bromine Determinations

Compound	Number of determinations	Mean error, %	
		Cl	Br
4-Chlorobenzoic acid	5	0.33	
4-Chloro-2,3-dinitrobenzene	4	0.33	
4-Bromobenzoic acid	7		0.29

In addition, by the same procedure the determination of sulphur in halogen--free compounds was performed in two ways: a.) with an absorption tube which had previously been used for halogen determination, and b.) with an absorption tube which has not been used for halogen absorption. In the former case the increase of weight corresponded to sulphur trioxide while in the latter it corresponded to sulphur dioxide (Table III). Hence, it follows that at high temperature (400^0) microquantities of either chlorine or bromine cause the quantitative oxidation of sulphur dioxide to sulphur trioxide.

TABLE III

Determination of Sulphur by Absorption on Lead Chromate in Halogen-Free and Halogen-Containing Absorption Tube

Compound		Found % S	
		Halogen-free absorption tube	Halogen-containing absorption tube
		calc'd. as SO_2	calc'd. as SO_3
Sulphanilic acid	18.51	18.54 (+ 0.03)	18.66 (+ 0.15)
Thiourea	42.12	42.43 (+ 0.31)	41.88 (— 0.24)
Methionine	21.49	21.86 (+ 0.37)	21.67 (+ 0.18)
N-Ethoxymalonyl-β-amino-γ-methylthiobutyric acid	11.56	11.56 (± 0.00)	—
1-Methyl-3-[2-(3′,5′-dinitro-benzoyl)-thioethyl]-indole	8.32	8.57 (+ 0.25)	—

When both halogen and sulphur are present, the increase in weight of the absorption tube is the combined weight of halogen and sulphur trioxide. Although such a weight gain will not permit the calculation of the percentage of either element, it would constitute evidence that the compound in question is pure and of the expected composition. For example, for S-benzylthiuronium chloride the mean errors from calculated values of 4 repeated results were: 0.21 for Cl and 0.57 for S.

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IZVOD

**Apsorbensi u mikroanalizi. III. Olovni kromat kao eksterni apsorbens
u mikroanalizi klora, broma i sumpora**

O. Hadžija

Opisana je jednostavna metoda za mikroodređivanje klora i broma, koja je izvediva s klasičnom mikroanalitičkom opremom. Halogeni se apsorbiraju na olovnom kromatu kod cca 400⁰. i određuju iz prirasta težine apsorbensa. Nađeno je također da kod 400⁰ mikrokoličine halogena kataliziraju kvantitativnu oksidaciju sumpornog dioksida u sumporni trioksid, što omogućuje pouzdanije određivanje sumpora. Kod poznatih spojeva koji sadrže sumpor i halogen (klor ili brom), iz sume težina sumpornog trioksida i halogena mogu se preračunati postoci sumpora i halogena.

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