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Studies on Microdetermination of Halogen and Sulfur in Organic Compounds. Tungsten Trioxide, a Novel Catalyst by Combustion Tube Method

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A new method of microdetermination of halogens and sulfur in organic compounds by combustion tube method was examined. It was found that tungsten trioxide among metal oxides was the most appropriate catalyst for oxidation of samples and air as carrier gas was suitable for the analysis. And also, direct introduction of few drops of water into the combustion system was found to be very effective for the analysis. Titration of halogens and sulfur in the combustion product were performed by argentimetric titration at pH 1 with dithizone indicator and by barium perchlorate titration at pH 2 using dinitrosulfonazo-III as indicator, respectively. Whole analysis procedure can be carried out only within 15 minutes.

Keywords——microdetermination of halogens; microdetermination of sulfur; combustion tube method; oxidation catalyst; tungsten trioxide; argentimetry; dithizone indicator; dinitrosulfonazo-III indicator

The oxygen flask combustion method[2] is widely used in routine analysis for determination of halogens and sulfur in organic compounds. However, there remain a couple of troubles, namely it takes at least half an hour to analyze one sample, and many flasks for numerous samples have to be provided in the analysis. On the other hand, dry combustion method using a stationary combustion tube is more appropriate for continuous analysis of samples because of its fast and simple procedure.

Use of some oxidation catalyst[3] such as platinum asbestos, lead chromate, vanadium pentoxide or a mixture of tungsten trioxide and vanadium pentoxide for filling in the combustion tube has been reported for microdetermination of halogens and sulfur in organic compounds.

In the process of our studies on organic elemental microanalysis, it was announced[4] that catalytic combustion method using a mixture of tungsten trioxide and zinc oxide was useful for the analysis of halogen and sulfur in organic compounds, particularly phosphorus-containing samples.

In this paper, an improved method for the rapid analysis is described.

One of the important factors in the analysis is that sample is rapidly heated up to desired temperature and is gently burned. It was found that uses of metal oxide as oxidation catalyst and air as carrier gas were suitable for that purpose. Of metal oxides, tungsten trioxide was the most useful catalyst.

Some difficulty was observed in the case of halogen analysis because volatile tungsten oxyhalogenate developed during the combustion of samples, but direct introduction of few drops of water into the combustion system to reduce the oxyhalogenate to hydrogen halide and tungsten trioxide completely solved this problem.

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1) Location: *2-2-1 Oshika, Shizuoka, 422, Japan.*
2) W. Schöniger, *Mikrochim. Acta*, **1955**, 123.
3) J. Horáček, V. Pechanec, and J. Körbl, *Collect. Czech. Chem. Commun.*, **27**, 1254 (1962); F. Scheidl, and V. Toome, *Microchem. J.*, **18**, 42 (1973).
4) K. Narita, Abstracts of Papers. 13th Annual Meeting of the Japan Society for Analytical Chemistry, Sendai, September, 1964, p. 98.

The titration was carried out under strong acidic medium to avoid interferance of other elements, namely determination of halogen is performed by argentimetric titration at pH 1 with dithizone indicator[5] and sulfur is determined by barium perchlorate titration at pH 2 using dinitrosulfonazo-III indicator.[6]

It is especially noteworthy that the whole analysis procedure can be carried out only within 15 minutes.

Experimental

Apparatus——A diagram of the apparatus is shown in Fig. 1. The apparatus consists of four parts, part of supplying of air, part of water introduction, part of sample combustion and absorption part of halogen or sulfur formed. Air, supplied from air pump (A), is led into a combustion tube (H) through a scrubber (B), a flow meter (C) and then a needle valve (D). Water is supplied from water pump (E)[7] and led into H through Teflon tube (F) and stainless steel tube (G).

A combustion tube made from quartz of 500 mm in length and 11 mm of outside diameter is surrounded by the sample furnace (I) and stationary furnace (J) and connected with absorption-tube (N) by ground joint (M). Tungsten trioxide granules (L) are packed in H at the center position of J of 100 mm in width and held with quartz wool from both sides. An absorption tube made from quartz of 100 mm in length and 11 mm of outside diameter is equipped with stop cock (O) and is packed with 3 mm diameter glass beads.

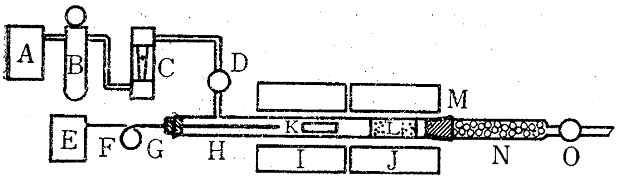

Fig. 1. Diagram of the Combustion Apparatus

A: air pump, B: scrubber, C: flow meter, D: needle valve, E: water pump, F: Teflon tube, G: stainless steel tube, H: combustion tube, I: sample furnace, J, stationary furnace, K: platinum boat, L: oxidation catalyst, M: ground joint, N: absorption tube, O: stop cock.

Preparation of Reagents and Solution

Tungsten Trioxide Granules——50 g of tungstosilicic acid hydrate and 2.5 g of asbestos were mixed with a small amount of water in porcelain crucible, then the mixture was heated over gas burner by stirring for complete dryness. The residue was granulated in 10—50 mesh and the granules were heated again at 800° for several hours. 40 g of pale yellow solid was obtained.

0.005 N Silver Nitrate Solution——0.85 g of silver nitrate was dissolved in 10 ml of water and added isopropanol up to 1000 ml.

0.01 N Barium Perchlorate Solution——1.95 g of barium perchlorate trihydrate was dissolved in 300 ml of water and isopropanol was added to the solution up to 1000 ml. The solution was adjusted to pH 2—2.5 with perchloric acid.

Dithizone Indicator Solution——The indicator was prepared by dissolving 10 mg of purified dithizone and 50 mg of diphenylcarbazide in 150 ml of acetone just before use.

Dinitrosulfonazo-III Indicator Solution——10 mg of dinitrosulfonazo-III (DOTITE) was dissolved in 10 ml of water.

Hydrazine Solution——1 g of hydrazine hydrate was dissolved in 1 ml of water.

Procedure

Combustion of Samples; For Determination of Halogens——Air is passed through the combustion tube from A while J is heated up to 800—850°. When the proper temperature is obtained the air flow is adjusted to 80 ml/min. After glass beads are wetted with lithium hydroxide solution, N is attached to H. 3—5 mg of the samples are weighed out into platinum boat(K) and K is placed in H at 5 cm away from the edge of J. The combustion is started when H is surrounded with hot sample furnace (I). Water is introduced into H one minute after the starting of the combustion, and the supplying of water is continued during a period of two minutes, while the water flow is adjusted to 0.15 ml/min. The combustion of sample is completely finished within five minutes. At the end of the combustion the air flow is stopped and N is taken off from H.

For Determination of Sulfur——A procedure for determination of sulfur was done in the same way for as the halogen determination, except changing of composition of absorption reagent and introducing of water. A mixture of an equal volume of 5% hydrogen peroxide and 1 N lithium hydroxide is suitable as absorption reagent for determination of sulfur, and there is no need to add water to the combustion system for the analysis.

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5) K. Narita, *Bunseki Kagaku*, **22**, 158 (1973).

6) N.N. Basargin and K.F. Novikova, *Zh. Analit. Khim.*, **21**, 473 (1966).

7) A little plunger pump is suitable for this purpose. Minimicropump S-2 (Takahashi Giken Glass Works Co., Ltd.) was used in the present work.

Titration Procedure of Halogens——Titration of halogen has been done by the procedure mentioned in the previous paper.[5]

Titration Procedure of Sulfur——Titration of sulfur was performed by the method of Basargin *et al.*[6] with a slight modification.

Results and Discussion

Absorption Reagents

A composition of absorption solution was examined for determination of chlorine in organic compounds according to the Pregl's catalytic combustion method using platinum contacts. The results are summarized in Table I. It was shown that alkaline solution could

TABLE I. Effect of the Composition of Absorption Reagents for Determination of Chlorine in *o,p'*-D.D.T.[a]

Flow rate of carrier gas (ml/min)	Composition of reagent	Amount of reagent	Chlorine found[b] (%)
10	2.5N NaOH 10 ml + 5% H_2O_2 1 ml	10 ml	50.43
10	2.5N NaOH 10 ml + 5% H_2O_2 1 ml	Amount for wet beads	50.55
10	1N NaOH 10 ml + 5% H_2O_2 1 ml	Amount for wet beads	49.63
10	0.1N NaOH 10 ml + 5% H_2O_2 1 ml	Amount for wet beads	50.00
10	5% H_2O_2	Amount for wet beads	38.42
10	5% H_2O_2	10 ml	39.56
10	2N LiOH	Amount for wet beads	49.78
10	2N LiOH 10 ml + 5% H_2O_2 1 ml	Amount for wet beads	49.88
10	1N LiOH 10 ml + 5% H_2O_2 1 ml	Amount for wet beads	50.38
10	0.1N LiOH 10 ml + 5% H_2O_2 1 ml	Amount for wet beads	50.36
10	0.1N LiOH	Amount for wet beads	50.15
30	0.1N LiOH	Amount for wet beads	50.51
50	0.1N LiOH	Amount for wet beads	50.17
100	0.1N LiOH	Amount for wet beads	49.91
150	0.1N LiOH	Amount for wet beads	50.06

[a] Combustion: Pregl's catalytic method, titration: potentiometric titration.

[b] Theoretical vlaue of chlorine in *o,p'*-D.D.T. is 50.01%, sample used is approximately 4 mg.

TABLE II. Analytical Results on Determination of Chlorine in *o,p'*-D.D.T. Using Several Oxidation Catalysts

Catalyst	Chlorine found (%)[a]							
	650°	700°	750°	800°	850°	900°	950°	1000°
Co_3O_4 (prepd. from oxalate)	47.23	48.52	47.95	46.52	45.76[b]			
Co_3O_4 (prepd. from nitrate)		49.20	49.00	48.51	48.71	49.54[b]		
CuO (prepd. from porous Cu)		45.01	45.24	48.31	47.60	43.41[b]		
CuO wire		38.44	40.87	41.62	41.85	40.44	40.04[b]	
Ni-asbestos				46.96	47.55	48.82	48.60	48.52[b]
Cr_2O_3-asbestos		45.63	47.95	48.16	47.66	48.23	48.64	48.78[c]
WO_3-asbestos			45.93	47.61	47.53	48.87	47.70	49.09
WO_3-asbestos (water added)	37.41	49.58	50.38	50.26	50.16	49.93	49.83	50.09
Pt-asbestos				48.73	49.15	49.07	49.97	49.77
Pt-quartz wool				40.99	44.59	47.59	44.16	39.94[c]
Quartz beads				44.28	49.06	49.66	50.00	49.84
Asbestos				44.61	46.63	47.48	48.47	49.81
Kashiwagi's combustion tube			48.74	50.42	49.87	49.54	49.82	50.27

[a] Sample used is approximate 4 mg, theoretical value of chlorine in *o,p'*-D.D.T. is 50.01%.

[b] Metal chloride was observed on the wall of the combustion tube.

[c] Adsorption of chlorine was observed.

satisfactorily absorb chlorine at higher concentrations than 0.1 N even in the carrier gas flow of 150 ml/min. It was also found that use of only hydrogen peroxide as absorption reagent was not sufficient for quantitative absorption of chlorine.

Oxidation Catalyst in the Combustion Tube

Ability of oxidation catalyst packed in the combustion tube was examined by the analysis of chlorine. The results are summarized in Table II. It was found that use of Kashiwagi's combustion tube[8] which belongs to the empty tube type as shown in Fig. 2 was effective at higher temperature than 800°. Quartz beads were useful catalyst at over 900°, but this catalyst was not sufficient for the analysis of large amounts of samples. Cobalt oxide on asbestos prepared by pyrolysis of cobalt nitrate or oxidative degradation of co-

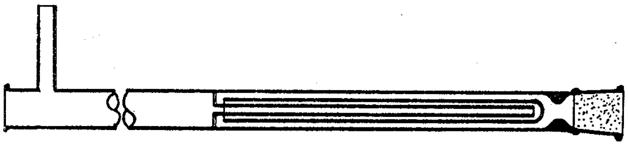
Fig. 2. Diagram of Kashiwagi's Combustion Tube

Table III. Effect of Volume of Added Water on Determination of Chlorine in *o,p'*-D.D.T.

Water volume (ml)[a]	Chlorine found (%)[b]	Water volume (ml)[a]	Chlorine found (%)[b]
0	47.53	0.3	50.06
0.1	48.81	0.5	50.08
0.15	48.52	1.0	50.14
0.2	49.45		

a) A water flow is adjusted at 0.1 ml/min.
b) Sample used is approximate 4 mg, theoretical value of chlorine in *o,p'*-D.D.T is 50.01%.

Table IV. Time and Period of Water Introduction into Combustion Tube for Determination of Chlorine in *o,p'*-D.D.T.

Combustion time (min)	Flow rate of air (ml/min)	Addition time for water[a] (min)	Chlorine found[b] (%)
10	50	0 —2	48.02
10	50	0 —3	48.68
10	50	0 —4	49.25
10	50	0 —5	49.77
10	50	0.5—2.5	50.09
10	50	1 —3	49.94
10	50	2 —5	49.44
10	50	5 —8	48.90
10	50	8 —10	48.73
6	50	1 —3	50.17
5	50	1 —3	49.90
4.5	50	1 —3	47.57
4	50	1 —3	44.98
7	30	1 —3	50.37
5	30	1 —3	48.54
5	80	1 —3	50.00

a) Water of 0.3 ml is added on each run during the listed period after the starting of the combustion.
b) Sample used is approximately 4 mg, theoretical values of chlorine in *o,p'*-D.D.T. is 50.01%.

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[8] H. Kashiwagi, Y. Tsukamoto, and M. Kan, Abstracts of Papers. 17th Annual Meeting of the Japan Society for Analytical Chemistry, Hiroshima, October, 1968, p. B380.

balt oxalate partly absorbed chlorine produced by combustion, therefore the cobalt oxide is not useful for oxidation of samples. The same phenomena as cobalt oxide were observed in the case of copper oxide, chromic oxide or nickel oxide.

It is well known that tungsten trioxide reacts with halogen to give tungsten oxyhalogenate which can be reduced into hydrogen halide and tungsten trioxide by water. As shown in Table II, tungsten trioxide was the most appropriate catalyst for determination of chlorine in organic compounds by the combustion tube method.

Addition of Water

Direct introduction of water into the combustion tube was a convenient and useful method in the analysis. The volume and period of water to be added were examined and the results are given in Table III and IV. It was shown that over 0.3 ml of water gave accurate values, and the desirable time for water addition was between one to five minutes after the starting of the combustion, so that the following conditions were set. A water flow is 0.15 ml/min and water is introduced for two minutes one minute after the starting of the combustion, while air flow is adjusted to 80 ml/min.

Temperature at the Tail End of the Combustion Tube

A temperature at the tail end of the combustion tube(H) should be kept at proper temperature in order to avoid condensation of halogens at the tail end. A temperature at the tail end was examined and it was found that the temperature over 250° gave satisfactory results in the determination of chlorine. For the determination of bromine, heating over 600° was required to avoid the condensation of bromine-compounds formed by combustion. Besides, the open end of the absorption tube(N) was placed at 1 cm inside from the edge of the stationary furnace(J), where temperature reached over 600°.

Medium of Barium Titration for Determination of Sulfur

It is known that ethanol or acetone is one of the suitable solvents in barium perchlorate titration using dinitrosulfonazo-III indicator. Effects of pH upon the end point error of sample solution in the method were investigated using various acids and the results as shown in Fig. 3 was obtained. Water contents in ethanol were examined and the results are shown in Fig. 4. From Fig. 3 and 4, it was found that perchloric acid was useful acid and 20—40% of water content in ethanol was suitable for the analysis, so that the method of barium perchlorate titration in this work is set as follows.

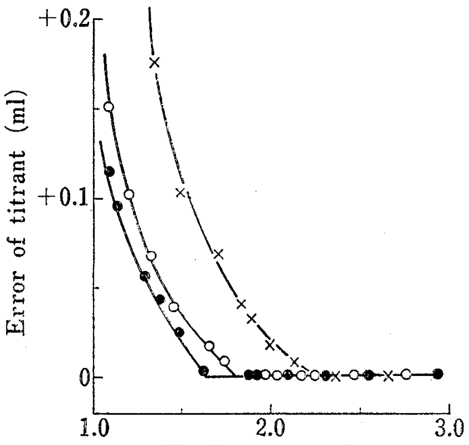

Fig. 3. Effect of pH upon the End Point Error of Sample Solution

—×—: HNO_3, —○—: HCl, —●—: $HClO_4$.

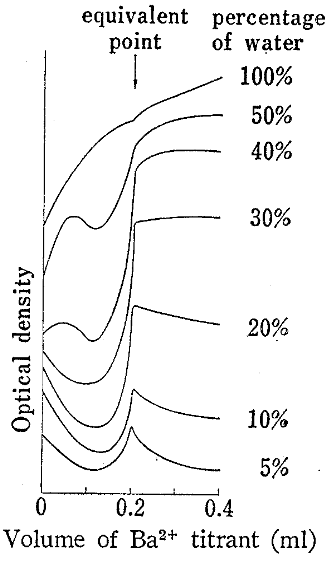

Fig. 4. Photometric Titration Curve *vs*. Water Content in Ethanol

Sample solution in 70% ethanol was adjusted to pH 1.6—3.0 with perchloric acid and the solution was titrated with 0.01 N barium perchlorate solution in 70% isopropanol using dinitrosulfonazo-III as indicator. A coefficient of variation is 0.25% when the determination of sulfur in approximately five mg of ammonium sulfate was repeatedly performed by the method.

Result of Analysis

Typical results from the determination of halogens and sulfur in the standard samples by the method are given in Table V.

It is shown in Table V that the method in this paper is very appropriate for the determination of halogens and sulfur in organic compounds with good accuracy. Further studies on determination of halogens in natural products, especially in marine sources are now in progress.

TABLE V. Analytical Results of Standard Samples

Sample	Calcd. (%)	n[a]	Found (%)[b]	σ (%)[a]	*c.v.* (%)[a]	ε (%)[a]
S-Benzylthiuronium chloride	Cl=17.49	5	17.56	0.15	0.86	0.068
p-Chlorobenzoic acid	Cl=22.64	5	22.70	0.09	0.43	0.043
Chlorobenzene	Cl=31.50	5	31.49	0.10	0.40	0.057
Kz. X[c]	Cl=32.98	5	32.97	0.13	0.45	0.067
o,p'-D.D.T.	Cl=50.01	5	50.00	0.16	0.32	0.072
p-Bromoacetanilide	Br=37.33	5	37.40	0.09	0.25	0.042
p-Iodobenzoic acid	I=51.17	5	51.06	0.16	0.32	0.072
S-Benzylthiuronium chloride	S=15.82	5	15.83	0.13	0.82	0.058
Sulanylamide	S=18.60	5	18.64	0.10	0.55	0.046
Dimethoate[d]	S=27.97	5	27.91	0.16	0.58	0.072
Allylisothiocyanate	S=32.34	5	32.34	0.18	0.56	0.081
Thiourea	S=42.12	5	41.98	0.12	0.27	0.051

a) n: number of run, σ: standard deviation, *c.v.*: coefficient of variation, ε: standard error.
b) Mean value of 5 runs.
c) Composition of Kz. X is $C_{15}H_{13}Cl_4OP$.
d) Composition of dimethoate is $C_5H_{12}NO_3PS_2$.