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Application of Ion-selective Electrodes for the Microdetermination of Chlorine and Bromine in Volatile Organic Compounds

By

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With 7 Figures

The results for the microdetermination of chlorine and bromine in highly halogenated volatile organic compounds with the oxygen flask method according to *Schöniger* are in many instances too low, because of incomplete combustion[1,2]. Several types of container for liquids have been used in the Schöniger method[1,3,4]. The use of thin polyethylene tubing is preferable to adhesive cellulose tape; the adhesive on the cellulose tape has a tendency to dissolve in the sample, resulting in a loss of the latter. Commercially available capsules (methyl cellulose, cellulose acetate and gelatin) have been found to have variable halogen blank values and their volume is too large for microanalysis.

Milligram samples of highly halogenated volatile compounds can be analysed by combustion tube method[2,5-7]. In each of these methods the final analysis is carried out in a step separate from the combustion.

Krijgsman et al.[8] have described a semi-automatic potentiometric method for organic halogen determination. The halide in the combustion gases is absorbed in 80% acetic acid and titrated with silver in the presence of an ion-selective Ag_2S electrode. A previously selected potential is taken for both the starting point and end-point of the titration. It was found, however, that the number of milligram samples which could be determined consecutively was limited because silver halide precipitates were formed; when about 18 μeq of chloride or bromide had been titrated,

adsorption of the halide on the precipitate occurred and low results were obtained; addition of tetraethylammonium perchlorate to the absorption solution did not fully prevent this co-precipitation.

An ion-selective Ag_2S electrode has also been applied by *Swartz* and *Light*[9] to the determination of S^{2-} and by *Papp* and *Havas*[10] for the determination of S^{2-}, $S_2O_3^{2-}$ and SO_3^{2-}; these authors used Hg^{2+} as titrant. Although the mechanism of the reaction of Hg^{2+} ions with the Ag_2S electrode is not fully clear, titrations of halides with Hg^{2+} have advantages over those with Ag^+ because Hg^{2+} ions form strong and soluble complexes with halides.

Experimental

Principle of the Determination

The sample is introduced by injection. After the combustion in an oxygen atmosphere over quartz and platinum at $1000°$, the halide is absorbed in 80% acetic acid containing some nitric acid, hydrogen peroxide and mercuric chloride or bromide.

The titration is carried out with Hg^{2+}. A selected potential between the reference and ion-selective electrodes is taken as both starting point and end-point for the titration.

Reagents

Absorption solution: a mixture of 80% acetic acid, 1.5% nitric acid, 1.2% hydrogen peroxide and 17.3% water, all v/v, plus 140 mg of $HgCl_2$ or $HgBr_2$ per 100 ml. This solution is kept in the dark.

Hg^{2+} solution, 0.1 N: 1.085 g of HgO dissolved in 100 ml of a mixture containing 80% acetic acid, 5% nitric acid and 15% water, all v/v. All reagents are analytical-reagent grade.

Apparatus

Fig. 1 shows a scheme of the apparatus used for combustion and titration. The sample is injected by way of septum *1* (Dohrmann 523–728). The injection port *2* (110 mm long, o. d. 10.5 mm), which is surrounded by a heating tape, contains an inner tube (73 mm long, o. d. 6.5 mm) filled with quartz wool. The combustion tube is completed by parts *3* (145 mm long, o. d. 22 mm) and *4* (80 mm long, o. d. 10.5 mm), the latter provided with a glass joint NS 7/16. The combustion tube is connected by means of a 2-mm capillary, surrounded by a heating tape *5*, to a cylindrical water-cooled absorption vessel[11] via a three-way stop-cock (2 mm bore). The double-junction reference electrode and the ion-specific electrode are placed in *6* (80 mm long, o. d. 12 mm) and *7* (85 mm long and o. d. 28 mm), respectively. Tube *8* (38 mm long, o. d. 8 mm) is located at the centre of chamber *9* (height 13 mm, o. d. 40 mm) which contains a Teflon-covered magnetic stirrer (22 mm long, o. d. 17 mm). The end of the 2-mm capillary, surrounded by a short piece of PVC tubing, is connected to the absorption vessel. All parts are made from Pyrex glass except for the quartz combustion tube. A 20-mm length

in the centre of the combustion tube is filled with platinum–quartz wool (Heraeus). Quartz granules are placed on each side as indicated in Fig. 1. The combustion tube was heated at 1000° by a Hereaus Rok 3/30 furnace (*10*). The titrant was added from a 600-μl burette (Ströhlein) through a polyethylene

quartz wool
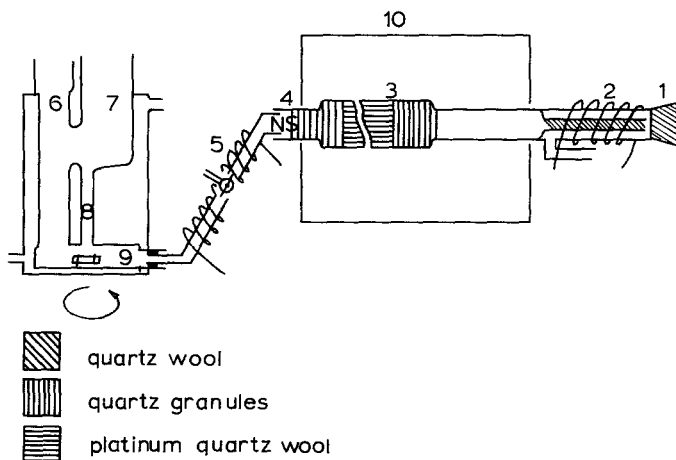
quartz granules

platinum quartz wool

Fig. 1. Combustion and titration apparaturs

capillary, the tip of which must be placed in tube *8* well below the electrode crystal surface. The mV readings were made on a Knick p_H-meter, range 140 mV, connected to a Kipp flat-bed recorder.

Electrodes: Ag_2S electrode (Orion 94-16); AgI electrode (Philips IS 550-I); Double-junction Ag/AgCl ref. electrode (Ingold 373-90-M 5 NS).
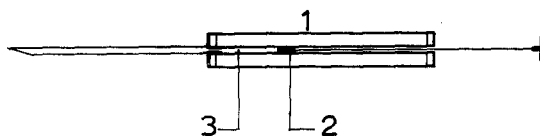

Fig. 2. Light-weight hypodermic syringe

Hypodermic syringe: a 10-μl syringe was used (Precision Sampling Corp., Baton Rouge, Louisiana). This syringe can be weighed to within 10 μg if gloves are used. A small hypodermic syringe (Fig. 2) was designed so that weighings to 1 μg could be made. It consists of a glass tube *1* (40 mm long, o. d. 3.5 mm) in which a capillary tube *2* (i. d. 0.5 mm, o. d. 1 mm) is centrally held. The piston is made from stainless steel and is provided with a Teflon tip *3* and an aluminium handle. A platinum needle (Hamilton KF 726 Pt, length outside the syringe 37 mm) is fixed in the capillary by means of Araldite. The syringe weighs about 0.8 g. In order to prevent loss of sample during transport and weighing, it is necessary that the sample be held in the glass capillary.

Procedure

Adjust the oxygen flow to about 10 ml/min. Turn the three-way stop-cock so that oxygen flows into the atmosphere, and fill the absorption vessel, which is cooled with tap water, with 25 ml of the absorption solution. Place both electrodes in the vessel and pass oxygen into it. Regulate the magnetic stirrer to give a fast circulation of the solution in the vessel and warm up heating tape 5 to 280°. After 15–30 minutes a constant potential of about 270 mV, which is taken as a set-point for the titration, is reached. Inject the sample into the quartz wool in front of tube 2 and warm its heating tape to about 130°. As soon as the halide enters the titration vessel the potential decreases. Add Hg^{2+} from the burette so that during the titration the potential is held to within $\pm$ 10 mV of the set-point. In this way the equilibrium potential will be reached more quickly. The titration is complete when not more than 0.1 μl of Hg^{2+} has to be introduced per minute.

Results

Results of chlorine and bromine determinations in some volatile substances are presented in Table I. Use was made of the light-weight syringe previously described or a 10-μl syringe for liquid samples and of a 1000-μl gas-tight syringe for CH_3Br.

Reversibility of the Ag_2S and AgI Electrodes with Respect to Hg^{2+}

The following experiments were done in order to test the reversibility of the Ag_2S and AgI electrodes. An Ag_2S electrode and a double-junction reference electrode were placed in 25 ml of an aqueous solution of nitric acid at p_H 1 or 2.7. Increasing quantities of Hg^{2+} were added and the corresponding potentials measured. Next increasing quantities of EDTA were introduced in order to complex the Hg^{2+} and the potentials were recorded again. The results are presented in Fig. 3. At p_H 2.7 the response appears to be reversible to lower Hg^{2+} concentrations than at p_H 1. This can be accounted for by the increased stability of the Hg–EDTA complex at p_H 2.7.

The experiment was repeated with the AgI electrode at p_H 1 (Fig. 4). Because Ag_2S is less soluble than AgI, Ag^+ from the AgI electrode is also available for complexing with EDTA. As a consequence, when the back-titration with EDTA is made an apparently irreversible reaction is observed. Similar measurements were also carried out in 80% aqueous acetic acid solution. Instead of back-titration of the Hg^{2+} with EDTA, increasing quantities of Cl^- were introduced (Fig. 5).

With the Ag_2S electrode measurements were also made in 25 ml of a 95% aqueous acetic acid solution containing some $HgCl_2$. Increasing
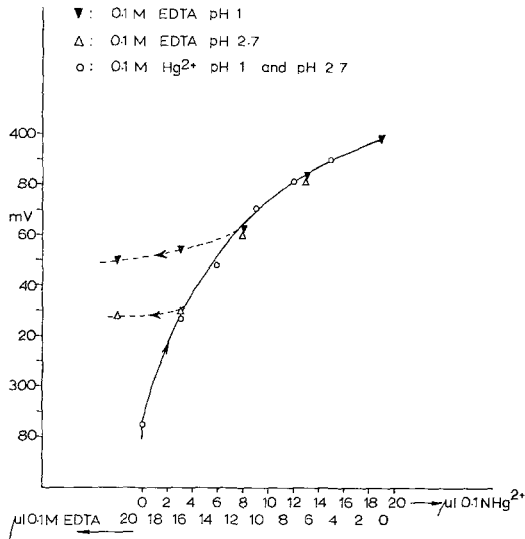
Fig. 3. Reversibility of the Ag_2S electrode in dilute nitric acid at pH 1 and pH 2.7 with respect to Hg^{2+}. The Hg^{2+} is back-titrated with EDTA
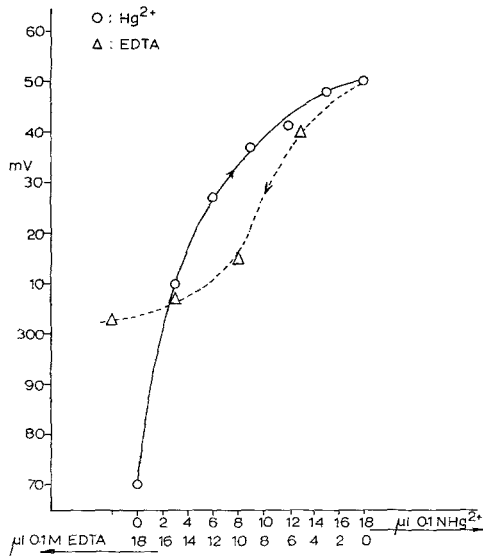

Fig. 4. Irreversibility of the AgI electrode in dilute nitric acid at pH 1 with respect to Hg^{2+}. The Hg^{2+} is back-titrated with EDTA

quantities of Cl^- and Br^- were introduced followed by a back-titration with Hg^{2+} (Fig. 6). Each experiment was repeated successively. As long as the concentration of Hg^{2+} is less than $10^{-3} M$ the durability and reversibility of the electrode are unaffected.
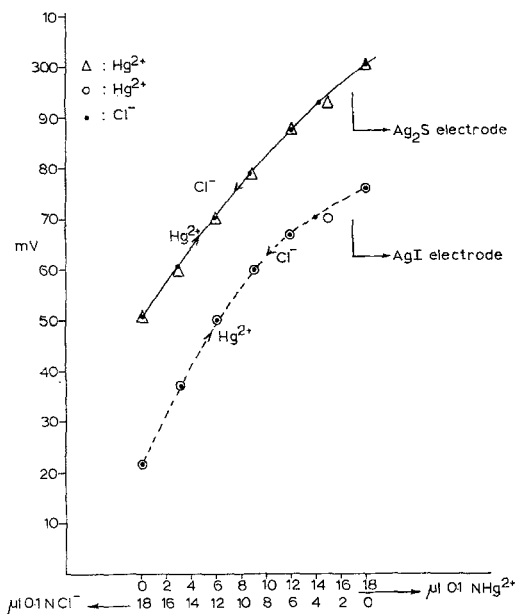

Fig. 5. Reversibility of the Ag_2S and AgI electrode in 80% acetic acid with respect to Hg^{2+}. The Hg^{2+} is back-titrated with Cl^-

Remarks and Discussion

The stability of the set-point potential of the titration is dependent on the quantity of water introduced; the latter should remain nearly constant. Therefore, the titrant was also prepared in an 80% acetic acid medium. The water originating from the sample has no noticeable influence on the measurements. In Fig. 7 is presented the change in the potential as a function of the $HgCl_2$ and $HgBr_2$ concentrations. If at least 30 mg of $HgCl_2$ or $HgBr_2$ are introduced to 25 ml of the absorption solution the potential is scarcely altered. The potential in both solutions is almost identical (ΔE is ca. 3 mV) so the same titration set-point can be used for both the Cl^- and Br^- determinations.

Introduction of nitric acid to the absorption solution and titrant is necessary to prevent precipitation of Hg^{2+} salts. It was found that a concentration of 1.5% v/v and 5% v/v nitric acid in the absorption solution and titrant respectively prevents this precipitation. With a concentration of 2% v/v of nitric acid in the titrant, precipitation occurs after two days.

Table I. Results

Substance		Boiling point °C	Sample, mg		Sample, µl		Halogen, %		Number of determinations	Relative standard deviation %
			min.	max.	min.	max.	theoretical	found		
CCl$_4$	(B. D. H. standard)	76.7	1.106	1.981			92.19	92.1$_3$	17	1.04
CH$_2$Cl$_2$	(Merck, "Uvasol")	39.7	1.311	2.292			83.56	83.4$_9$	5	1.04
C$_2$Cl$_4$	(Merck, "Uvasol")	121	1.362	2.080			85.52	85.6$_7$	2	
CHCl$_3$ *	(Merck, p. a.)	62	1.75	1.85			89.10	89.2$_4$	10	1.29
C$_2$H$_5$Br	(Merck, "for synthesis")	38.4	1.767	2.365			72.55**	72.1$_6$	7	1.44
CH$_3$Br	(Baker, 99.5% purity)	4.5			150	900	83.74	83.6$_8$	5	1.02
CHBr$_3$	(B. D. H., GLC standard)	150	2.295	3.383			94.85	95.5$_5$	5	0.82

* Injected with a 10-µl syringe which is weighed on a 10-µg balance.
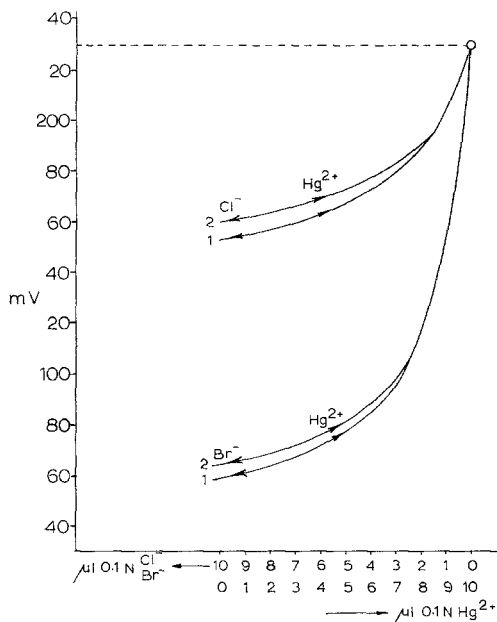
** Determined by the Schöniger flask method.

Fig. 6. Reversibility of the Ag₂S electrode with respect to Cl⁻ and Br⁻ in 95% acetic acid. The halide is back-titrated with Hg²⁺
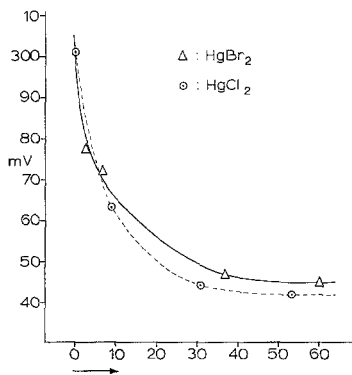

Fig. 7. Change in potential as a function of the $HgCl_2$ and $HgBr_2$ concentration in the initial absorption solution

The use of reducing agents stronger than H_2O_2 in the absorption solution results in a reduction of the Hg^{2+} ions. If the concentration of H_2O_2 is greater than 1.2% v/v then there is oxidation of the S^{2-} ions from Ag_2S the crystal.

Titrations with Hg^{2+} with the use of solid-state silver halide electrodes have also been mentioned in the literature[12,13]. It was reported[13] that the AgI electrode is more suitable for mercury than the Ag_2S electrode. Therefore, some determinations were carried out with the AgI electrode but it was found that the response time was very slow when compared to that of the Ag_2S electrode.

The maximum sensitivity and accuracy of the titration is about 0.03 μeq of halide/mV. There is a linear relationship between the quantity of organic Cl combusted (up to 3 mg) and the quantity of Hg^{2+} required for the back-titration.

Some experiments were also made in an attempt to clarify the mechanism of the interaction of Hg^{2+} ions with the Ag_2S electrode. A 1-electron Nernst slope of 60 mV was observed with Hg^{2+}. This behaviourt can be explained if it is assumed that the following ion-exchange process occurs on the surface of the Ag_2S crystal:

$$Hg^{2+} + Ag_2S_{(crystal)} \rightleftharpoons [AgHgS]^+_{(crystal)} + Ag^+.$$

X-Ray fluorescence measurements carried out on the surface of an Ag_2S crystal showed that mercury can be detected after the crystal has been in contact for some time with a dilute Hg^{2+} solution. Before this measurement was made the crystal had been placed for some hours in 0.1 M EDTA and then rinsed with water and acetone. The intensity of the mercury signal is not affected even after treatment for several weeks with EDTA. Diffusion of mercury in the crystal does not occur. When the crystal surface is repolished with silicon carbide emery paper (number 400) the mercury response disappears.

Acknowledgements

Summary

Application of Ion-selective Electrodes for the Microdetermination of Chlorine and Bromine in Volatile Organic Compounds

A method is described for the determination of chlorine and bromine in mg samples of highly halogenated volatile organic compounds. The samples are introduced into the combustion system by injection and burnt in a stream of oxygen at 1000° over platinum and quartz. The combustion gases are absorbed in a solution of 80% acetic acid containing some hydrogen peroxide, nitric acid and mercuric chloride or bromide.

The halide is then titrated with mercury. The end-point is determined by an ion-specific electrode. One determination takes approximately 15 minutes. The relative standard deviation of the determination is about 1%. The reversibility and durability of the silver sulphide electrode are unaffected as long as the mercury ion concentration is less than 10^{-3} M.

Zusammenfassung

Eine Methode für die Bestimmung von Chlor und Brom in Milligramm hochhalogenierter Substanzen wird beschrieben. Die Proben werden in das Verbrennungssystem eingespritzt und in einem Sauerstoffstrom bei 1000° C über Platin und Quarz verbrannt. Die Verbrennungsgase werden in 80% Essigsäure absorbiert, die etwas Perhydrol, Salpetersäure und Quecksilber-chlorid oder -bromid enthält. Das Halogen wird mit einer Quecksilber(II)-lösung titriert. Der Endpunkt wird mit Hilfe einer ionenspezifischen Elektrode ermittelt. Eine Analyse dauert etwa 15 Minuten. Die relative Standard-abweichung ist $\pm$ 1%. Die Reversibilität und Dauerhaftigkeit der Silbersulfid-elektrode bleibt so lange unbeeinflußt, als die Konzentration der Quecksilber-ionen geringer ist als 10^{-3}-m.

Résumé

Une méthode pour le dosage du chlore ou du brome dans des échantillons milligramiques de composés organiques volatiles contenant des quantités élevées d'halogène a été décrite. Les échantillons sont introduits dans le système de combustion par injection et la combustion s'effectue sous courant d'oxygène à 1000° C sur platine et quartz. Les gaz de combustion sont absorbés dans une solution d'acide acétique 80% avec addition de faibles quantités de peroxyde d'hydrogène, acide nitrique et chlorure ou bromure mercurique. Puis l'haloide est titré avec une solution mercurique. Le point d'équivalence est établi à l'aide d'une électrode ion-spécifique. Un dosage prend approximativement 15 minutes et l'écart type est environ 1%. La réversibilité et la durabilité de l'électrode de sulphure d'argent restent intactes pourvu que la concentration mercurique ne surmonte pas celle de 10^{-3} M.

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