

Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday

## A NEW APPROACH FOR THE DETERMINATION OF ORGANOBROMINE IN HARMFUL WASTE

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### Abstract

Determination and estimation of organic sulphur, nitrogen, phosphor and halides in harmful chemical waste and estimation of emission of SO<sub>2</sub>, NO<sub>x</sub>, HCl, HBr or HI during incineration are the primary task of risk assessment. In our paper we present a new analytical approach for determination of bromine in a heterogeneous sample. The method applied is based on combustion of chemical waste under oxygen atmosphere (pressure 20 bars) and transformation to corresponding anions. These anions can be measured by ion chromatography. Using this method all hetero atoms can be transformed to corresponding anions (except for oxygen) and can be measured by ion chromatography. In this paper we report of determination of bromine content of chemical waste. During the combustion of organobromine compounds different types of inorganic bromine are formed. All types of bromine must be converted to Br<sup>-</sup>. To fulfil it the above, ascorbic acid solution was used for absorbing and transforming all types bromine compounds to Br<sup>-</sup>. We will discuss all the details about this new approach and give all the parameters to get efficient conversion from organic bromine to bromide anions.

**Keywords:** absorption, ascorbic acid, chemical waste, combustion, ion chromatography, reduction

### Introduction

In chemical industry a huge amount of chemical waste is produced. This waste can be deposited or must be incinerated. Before incineration the composition of the materials has to be determined. The primary aim is to get data about organic sulphur, phosphorous, nitrogen and halide content of waste. In the past there were several different aspects to get sufficient data for this pursue. Combustion methods are used in two different ways. In the first one the residue of combusted is analysed. In the second one combustion products of non metallic elements are collected in a suitable absorption solution then analysis of the absorber solution can be made by ion chromatographic technique. This approach was successfully used for the determination of halides (to form such products as HF, HCl, HBr and HI) and sulphur and phosphor which can be formed SO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub> [1-3].

During the dry ashing the formed volatile compounds are evaporated and this method can be applied if the solutes are non volatile. The dry ashing method can be used mainly for the determination of metal content of waste. The simplest apparatus for combustion of organic samples is a Schoninger flask method. Combustion can be made under oxygen at atmospheric pressure and the combustion product of the sample is absorbed in a solution with given composition. The sample size is limited by the amount of oxygen.

In par oxygen bomb combustion can be used to as high amount of sample as 1 g. Absorption of products formed during the combustion takes time. In some cases not only one compound is formed, but more oxidised products also such as HBr, HI, HBrO<sub>3</sub> and HIO<sub>3</sub>. In such cases a reducing agent as hydrazine sulphate [1–3] should be added to the absorber solution so that only bromide and iodide are present in the final solution.

There are some other publications for the determination of bromine in organic reagents [4, 5], in polymers [6] and biological samples [2]. In our new approach we present all the details about determination of bromine in chemical waste and about using a new reducing agent in absorption liquid. This new compound is ascorbic acid.

## Experimental

### Materials

High purity water was produced by MilliQ (Waters, Milford, USA); acetophenone was kindly donated by Chinoin Chemical Works, (Chinoin, Budapest, Hungary); acetonitrile, methanol (Merck, Darmstadt, FRG); borate/gluconate eluent Take a one litre flask and add 16 g sodium gluconate, 18 g boric acid, 25 g sodium tetraborate decahydrate, add approximately 500 cm<sup>3</sup> high purity water, and mix thoroughly until dissolution of solids, then add 250 cm<sup>3</sup> of glycerine. Fill the flask to the mark with high purity ( $S < 0.1 \mu\text{S}/\text{cm}$ ) water and mix thoroughly. The concentrate can be stored in refrigerator up to six months. Take an other one litre volumetric flask and pour 500 cm<sup>3</sup> high purity water, then add 20 cm<sup>3</sup> borate/gluconate-concentrate, 20 cm<sup>3</sup> concentrate, 20 cm<sup>3</sup> *n*-butanol and 120 cm<sup>3</sup> acetonitrile. Fill the flask to the mark with high purity water and mix thoroughly. Before using this eluent, filter through a 0.45  $\mu\text{m}$  membrane filter (laboratory prescription); ascorbic acid (Merck, Darmstadt, FRG); SepPack C-18 cartridge (Waters, Milford, USA).

### Equipment

The ion chromatographic system was a single column ion chromatographic one, consisting of a Waters 501 high pressure pump (Waters, Milford, USA) a Rheodyne 7125 sample valve equipped with 20  $\mu\text{l}$  sample loop (Rheodyne, Cotati, USA) Ionpack A 50X4.6 mm (Waters, Milford, USA) conductivity detector,

Waters 430 CD (Waters, Milford, USA) data handling Waters 740 (Waters, Milford, USA). The combustion bomb is produced in our institute [7].

### Sample treatment

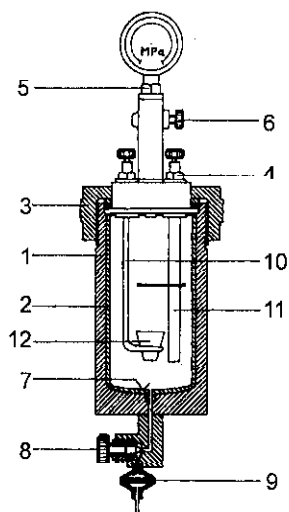
Before the determination of organobromine content of chemical waste the inorganic bromide and chloride content of the samples was determined. For this purpose approx. 2 ml of samples were measured (about 2.2 g) and put into a separation funnel, 20 ml high purity water was added and the sample was extracted twice (about 5–10 min). After we centrifuged the samples for 5 min, about 3 ml was taken from the upper phase with an automatic pipette and it was cleaned on a SepPack C-18 cartridge. First portion of eluate was discarded and the second part of the cleaned sample was applied to the ion chromatographic equipment.

### Activation of SepPack C-18 cartridge

The SepPack C-18 cartridge was washed with 2 ml of methanol and 2 ml of high purity water. Every SepPack C 18 cartridge was used only for one sample.

### Combustion of sample

The sample was combusted in a home made combustion bomb, the combustion bomb and the procedure are described in a Hungarian patent [7]. The structure of the combustion bomb is given in Fig. 1. Sample was taken to a halide free



**Fig. 1** Scheme of combustion bomb with absorption solution. Symbols: 1 – house, 2 – insert, 3 – upper part, 4 – electrical connection, 5 – pressure gauge, 6 and 8 valves, 7 – absorption solution, 9 – filter, 10 – sample holder rod, 11 – tube for oxygen, 12 – sample holder

paper and placed into the holder, which contained the absorbers. The bomb was washed with oxygen about 10 times of its volume and pressurised to 20–40 bars. After ignition the bomb was shaken for about 5 minutes. The filtered solution was applied to an activated SepPack C-18 cartridge, approx. 0.5 ml was discarded and the following 0.5 ml was injected to ion chromatograph.

### Validation of combustion. Determination of reaction time

During combustion of organobromine compounds several forms of bromide can be formed. For example  $\text{Br}_2$ ,  $\text{HBrO}_3$ , and so on. It is impossible to measure of all forms of them, therefore a conversion to bromide must be done. For this purpose we used a well-known chemical reaction given in Fig. 2.

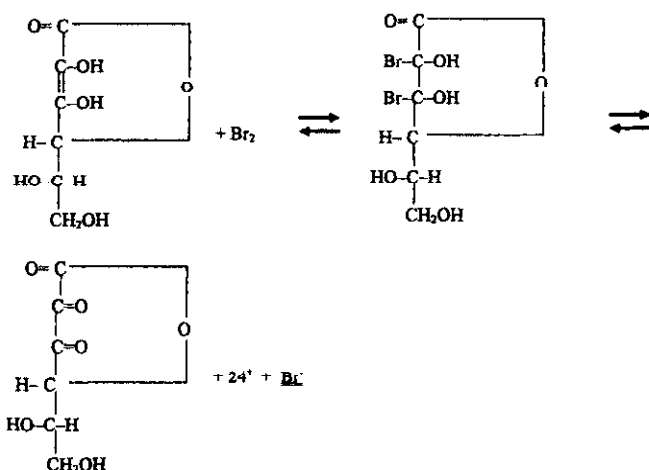


Fig. 2 Reaction scheme of reduction of  $\text{Br}_2$  formed during the combustion

According to the reaction scheme there are two steps. This reaction at atmospheric pressure needs some time. To control this one we analysed the samples at different times after absorption. For modelling the reaction bromo-benzene was used as a test compound. In our experiments 7.4 and 14.9 mg 2-bromo-acetophenone were measured onto an anion-free paper and placed into the combustion bomb. The volume of absorbing solution was  $25 \text{ cm}^3$  and the concentration of ascorbic acid was  $0.05 \text{ mol dm}^{-3}$ . Results are summarised in Table 1.

Based on our results about 5 minutes of reaction time is long enough to get maximum conversion.

### Determination of maximum amount of bromo-acetophenone

Different volumes of 2-bromo-acetophenone were measured onto anion-free paper, combusted and the bromine content of the absorption solution was deter-

**Table 1** Effect of reaction time on determination of bromine in organic compounds

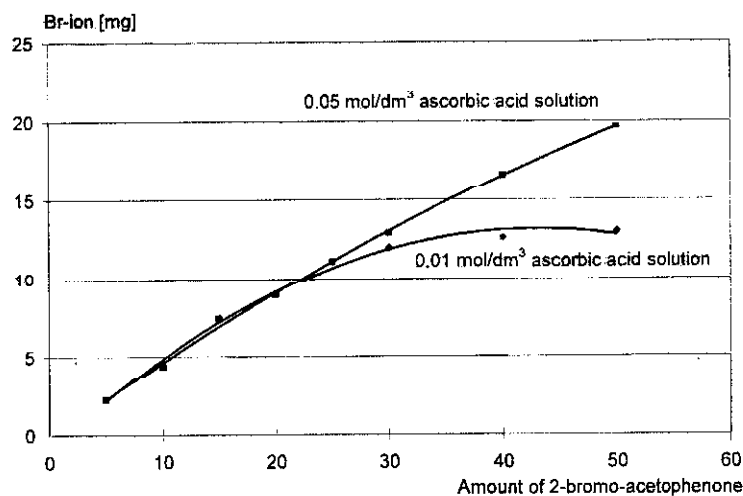
| Number of experiment | Amount of sample/mg | Reaction time/min | Recovery/% |
|----------------------|---------------------|-------------------|------------|
| 1                    | 7.4                 | 0                 | 85.9       |
| 2                    | 7.4                 | 5                 | 102.3      |
| 3                    | 7.4                 | 10                | 103.1      |
| 4                    | 7.4                 | 15                | 103.2      |
| 5                    | 10.4                | 0                 | 80.0       |
| 6                    | 10.4                | 5                 | 91.2       |
| 7                    | 10.4                | 10                | 95.3       |
| 8                    | 10.4                | 20                | 97.1       |
| 9                    | 10.4                | 30                | 98.3       |

mined. The absorption solution was 50 times diluted with ion chromatographic eluent. Results of these experiments are summarised Fig. 3.

It could be concluded that using  $0.01 \text{ mol dm}^{-3}$  ascorbic acid absorption solution the highest amount of 2-bromo-acetophenone is about 45 mg. Using  $0.05 \text{ mol dm}^{-3}$  ascorbic acid absorption solution, amount of 2-bromo-acetophenone could be higher than 50 mg.

#### *Determination of limit of detection and limit of quantitation*

The limit of detection was  $0.1 \mu\text{g ml}^{-1}$  bromide in absorber solution at signal to noise ratio of 3, and  $0.3 \mu\text{g ml}^{-1}$  for limit of quantitation ( $S/N \geq 10$ ). Using 10 ml of absorption solution and amount of sample 40 mg; 0.025% of organo-bromine can be detected and 0.075% can be determined.

**Fig. 3** Effect of 2-bromo-acetophenone amount on recovery of  $\text{Br}^-$  ion in absorption solution

### *Analysis of chemical waste*

The chemical waste contained organochlorine and bromine. The first step is to control the chloride and bromide content of chemical waste. In Fig. 4 a chromatogram from extraction solution of chemical waste can be seen. 40 mg waste was extracted with 10 ml of high purity water twice. It can be seen that no inorganic anions are present in the waste. 40 mg of waste was combusted in the reactor and the result is shown in Fig. 5. In the chromatogram two ions can be identified chloride and bromide. This chemical waste was a residue of the production of 2-bromo-acetophenone. The amount of chlorine was  $35 \text{ mg g}^{-1}$  and the amount of bromine was  $51 \text{ mg g}^{-1}$ .

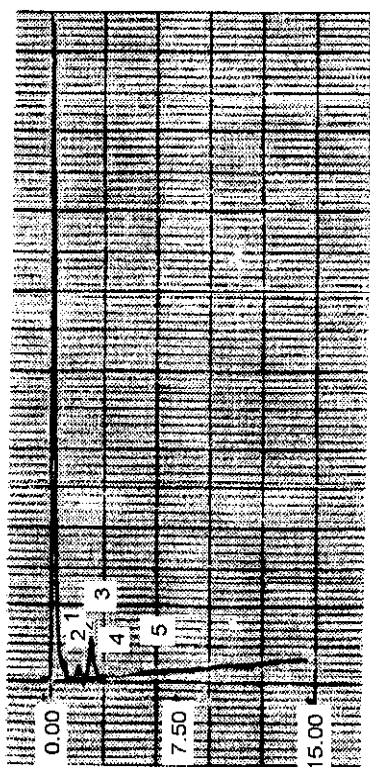


Fig. 4 Determination of bromide in the waste. Extraction was done with high purity water. Ion chromatograph was single column ion chromatography. Eluent: borate/gluconate

### **Conclusions**

Determination of organobromine in chemical waste can be made with combustion bomb containing ascorbic acid absorption solution. Ascorbic acid re-

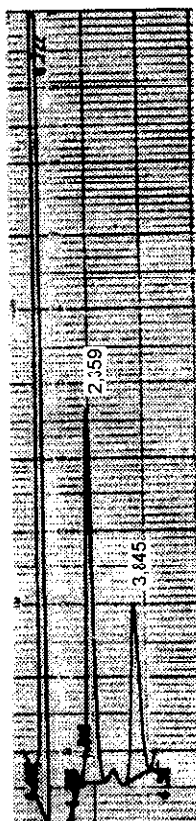


Fig. 5 Determination of organobromine and chlorine in the waste. Retention times are 2.4 min for chloride, and 3.85 min for bromide. Other conditions see in Fig. 4

duces different forms of bromide to  $\text{Br}^-$  and the concentration of this solute can be determined by ion chromatography. At the same time under verified pressure and in reductive solution chlorine is also absorbed. This reductive method is known in the classical analytical chemistry but it has not been applied in combustion chemistry and for the determination of organobromine yet. The amount of sample analysed depends on volume and concentration of the ascorbic acid solution. Using about 10–20 ml  $0.05 \text{ mol dm}^{-3}$  ascorbic acid solution as absorption liquid approx. 40–50 mg sample can be used for determination of organobromine content of the waste.

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