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# Determination of Organic Group Parameters: (AOCl, AOBr, AOS) in Water by Means of Ion-Chromatographic Detection. Pyrohydrolysis and Absorption

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**Dedicated to Professor W. Haerdi on the occasion of his 60th birthday**

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In recent years methods have been developed to determine organic halogen at the  $\mu\text{g/l}$  level in water samples by adsorbing these compounds on active carbon and by detecting the inorganic halides formed after conversion of the adsorbates by pyrohydrolysis. Applying these techniques the analysis of the so-called group parameter "Adsorbable Organic Halogen (AOX)" is performed.

The distinction of each of the halogens in the group parameter AOX and the determination of the parameter "adsorbable organic sulfur compounds (AOS)" can be realized using ion-chromatography for the detection of the anions, obtained after pyrohydrolysis of the adsorbed organic compounds.

Further investigations have shown good adsorption capacity of a newly developed nearly chlorine- and sulfur-free active carbon for organic model substances. This report presents the examinations concerning pyrohydrolysis of the organic solutes and absorption of the formed inorganic species.

The conditions for complete conversion of the model substances and high recovery rates in inorganic anions have been proved successfully. The optimization of the

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pyrohydrolysis apparatus and of the combustion conditions have been performed and proved with good results.

**KEY WORDS:** Water, group parameters, AOCl, AOB<sub>r</sub>, AOS, ion-chromatography, organohalogens, organosulfur compounds.

## INTRODUCTION

Since the detection of haloforms and other halogenorganic compounds in drinking water, there is a growing interest in their source, toxicity, identification and quantitation. Because many of such compounds are unaccounted by methods designed to identify individual substances several authors have described the analysis of organic halogens as a group parameter.<sup>1-8</sup>

For the determination of organic sulfur in addition to the halides Schnitzler prepared nearly chlorine- and sulfur-free charcoal from sugars.<sup>7</sup> By performing this technique the Merck Company (Darmstadt, FRG) has produced this active carbon for analytical application.

We started our work investigating the adsorption capacity of various charcoals for selected organic model substances. To avoid the undesirable adsorption of inorganic anions, like chloride and sulfate on the active carbon the experimental procedure has been optimized.<sup>9</sup>

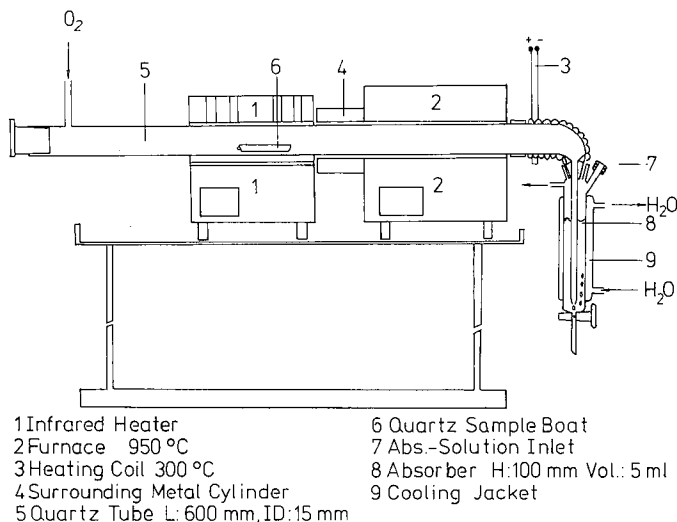
The determinations of inorganic anions have been performed by means of ion-chromatography applying indirect UV-detection. This technique and the results for anion determination have been described elsewhere.<sup>10-12</sup>

Following this way the experimental conditions of the absorption of the formed inorganic ions and the pyrohydrolysis have been optimized:

- assembly of a first pyrohydrolysis apparatus;
- absorption of HCl, HBr, H<sub>2</sub>SO<sub>4</sub>;
- pyrohydrolysis of the model substances: 4-chlorophenol (p-ClP), 4-bromophenol (p-BrP), 4-bromobenzoic acid (p-BrBA), thiobenzamid (TBA), toluenesulphonic acid (TSA);
- modification of the pyrohydrolysis apparatus.

**EXPERIMENTAL**

The first utilized pyrohydrolysis apparatus is shown in Figure 1. For the pyrohydrolysis equipment an electric furnace Model D-02/GTE and an infrared heater Model I-04/RP with temporal temperature programming (Ströhlein GmbH, Kaarst, FRG) have been used.



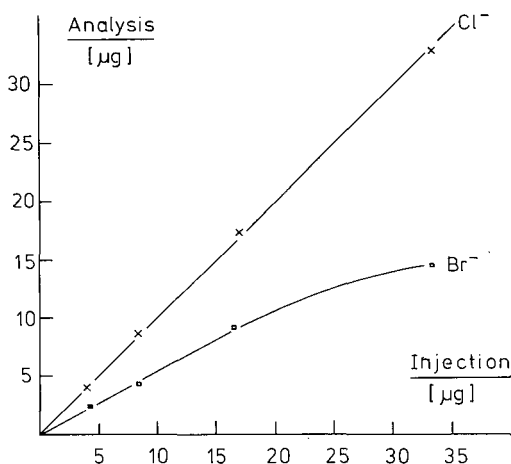
**Figure 1** Pyrohydrolysis apparatus.

**Conversion and absorption of inorganic acids**

The absorption of the hydrogen halogenides and sulfur oxides could be proved using the mineralic acids, from which diluted solutions have been transferred into the sample boat and converted under pyrohydrolysis conditions. The conditions of the German standard method for the AOX-determination have been chosen.<sup>13</sup>

This procedure is advantageous, because the dependence of the formation of the inorganic ions on the pyrohydrolysis conditions can be excluded. Further we have been able to detect a possible decomposition of the mineralic acids.

The analyzed contents of chloride and bromide in the absorption



**Figure 2** Recovery of HCl and HBr. Conditions: Furnace, 950°C; Infrared heater: Drying, 3 min, 120°C. Oxidation: 5 min, 950°C. Cooling: 2 min. Reaction time: 10 min. Flow O<sub>2</sub>: 100 ml/min. Abs. Sol.: H<sub>2</sub>O pH 8.

solution compared with injected contents is demonstrated in Figure 2. This shows a good recovery of hydrogenchloride while a loss of hydrogenbromide is observed.

No concentrations of sulfate in the absorption solution have been determined, if H<sub>2</sub>SO<sub>4</sub>-solutions have been converted in the pyrohydrolysis apparatus. The reasons for this behaviour of sulfuric acid could be explained by experiments discussed in a further chapter.

For the loss of bromide anion a partial oxidation of the hydrogenbromide in the oxygen stream may be responsible. Although working with inert gas like argon no higher yields of bromide formation will be reached. With increasing pH-values up to 10 of the absorption solution recovery rates of 80% for bromide have been achieved.

The resulting recovery rates for bromide are independent on the volume of absorption solution in the absorber.

An additional increase of bromide formation has been reached using absorption solution containing hydrazine hydroxide. This reducing agent has been used by several authors.<sup>5,14,15</sup>

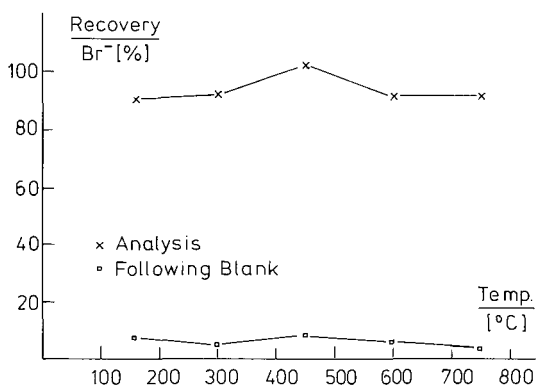
But studies of Gilbert have shown an auto oxidation of hydrazine in the presence of air, respectively, oxygen under formation of hydrogen peroxide in alkaline solutions.<sup>16</sup> Alkaline hydrogen per-

oxide containing solutions have been used to oxidize sulfur compounds into sulfate and a bromide formation has been performed too.<sup>7,14,17</sup> The oxidation power of hydrogen peroxide in alkaline solution is sufficient to oxidize sulfite to sulfate, but it seemed that the unknown bromine species could be reduced to bromide.

Figure 3 shows the influence of temperature in the pyrohydrolysis apparatus on the recovery of bromide using an inert argon gas stream. Injecting HBr-solution in an analysis run overall, a 90% recovery rate has been reached.

After each analysis a blank value has been determined and a leaching of bromine species out of the pyrohydrolyser has been observed. The recovery rates of the analysis and blank in summary has been nearly 98% and the loss of bromide by decomposition has been negligible. For temperatures lower than 450 °C there has been a condensation effect, an increase of recovery greater than 100% supports this behaviour. For higher temperatures the blank values have decreased, but could not be neglected. An absorption of bromine species from the quartz tube has been indicated even at higher temperatures and has been responsible for the blank values. With growing analysis times the blank values could be reduced accompanied by an increase of the recovery rate of bromide.

With absorption solutions containing hydrogen peroxide good recovery of bromide and chloride have been achieved too.



**Figure 3** Recovery rates and blanks for HBr. Conditions: Furnace, 950 °C. Infrared heater: Drying, 3 min, 120 °C. Oxidation: 9 min, 950 °C. Cooling: 3 min. Reaction time: 15 min. Flow Ar: 100 ml/min. Abs. Sol.: H<sub>2</sub>O pH 9 + 4 mg/l N<sub>2</sub>H<sub>4</sub>. Sample content: 10 µg Br<sup>-</sup>.

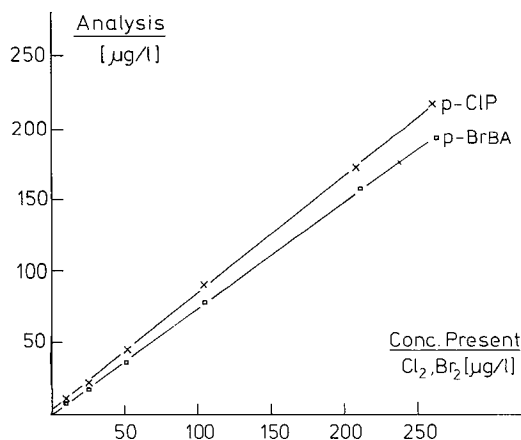
### Conversion of halogenorganic model substances

For proving the pyrohydrolysis of the organic compounds: 4-chlorophenol (p-CIP), 4-bromobenzoic acid (p-BrBA) or 4-bromophenol (p-BrP) have been chosen. Recovery rates greater than 95% have been obtained if 50–200  $\mu\text{l}$  of stock solutions with concentrations of 200 mg/l have been injected into the quartz boat and have been pyrohydrolysed.

Based on these promising results a calibration procedure for AOCl and AOBr analysis as described in the German standard method has been performed.<sup>13</sup> The Mitsubishi active charcoal TOX70 (Mitsubishi Chemical Industries Ltd., Japan) has been used for the enrichment of the model substances by shaking the 100 ml samples with 50 mg of active carbon for one hour.

The analysed concentration values have been plotted against the present concentration values (Figure 4). The data for the linear regression are demonstrated in Table 1 and have been calculated using the German standard methods for examination of water, waste water and sludge.<sup>18,19</sup> The blanks have been 11.6  $\mu\text{g/l}$  for chloride and 2.2  $\mu\text{g/l}$  for bromide and were subtracted from the ion-chromatographic anion determinations of the absorption solutions.

Good results have been achieved for the linear regression coefficients, calculated blanks and standard deviation of the method. The



**Figure 4** Calibration plot of AOX-analysis for p-CIP and p-BrBA using TOX70 active carbon for enrichment. Conditions: See Figure 3. Flow  $\text{O}_2$ , 100 ml/min.

**Table 1** Statistical characteristic of AOC1<sup>-</sup> and AOB1<sup>-</sup> calibration

<i>Parameter</i>	<i>LRC</i>	<i>Slope</i>	<i>BL cal</i> ( $\mu\text{g/l}$ )	<i>RSDM</i> (%)
AOC1 (p-CIP)	0.9999	0.8265	1.88	1.78
AOB1 (p-BrBA)	0.9998	0.7437	-0.44	2.21

Abbreviations: LRC—Linear regression coefficient. Slope—Slope of calibration plot. BL cal—Calculated blank. RSDM—Relative standard deviation of the analysis method.

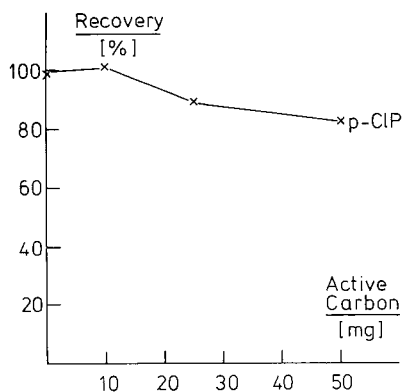
difference between the determined slopes and the theoretical slope values of 1 are indicating a low recovery for AOC1 and AOB1 in the working range. The experiments performed for testing the adsorption capacity of the active carbon TOX70 represented nearly quantitative adsorption of the model substances.<sup>9</sup> Therefore the loss of recovery for AOC1 and AOB1 may be caused from the pyrohydrolysis procedure. Because the TOX70 active carbon has a sulfur content of 0.50%, the formation of sulfate has been observed additional to these calibration procedures. The blanks of sulfate have been in the range of 20–50 mg/l.

Therefore two effects could be responsible for the loss of chloride and bromide during the pyrohydrolysis. First the excess of carbon dioxide, arising from the combustion of the charcoal and secondly the high sulfur content of the carbon, which has to be converted too at the same time as the adsorbed model compounds have to be oxidized.

Proving this, sources of p-CIP stock solution have been pipetted on different amounts of active carbon which have then been pyrohydrolysed. The experiments have proved the expected effect of the charcoal (Figure 5).

Following the thermal desorption of substances from the active carbon has been examined. The desorption of hydrogenchloride with increasing temperatures is shown in Figure 6. Good recovery of chloride is achieved for temperatures above 400 °C, but the charcoal is ignited and has burned off in the oxygen stream. For thermal desorption of organic compounds higher temperatures have been necessary and avoiding the ignition of the charcoal inert gas streams too.<sup>20</sup>

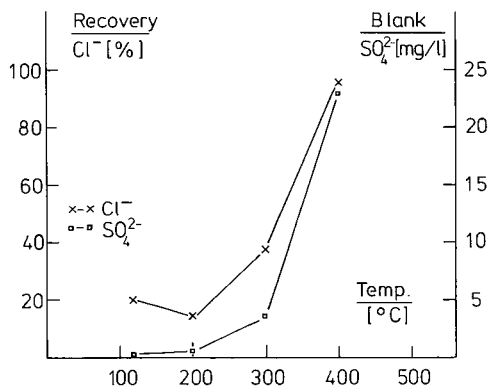




**Figure 5** Pyrohydrolysis of TOX70 active carbon loaded with p-ClP. Conditions: Reaction time 15 min (see Figure 3). Flow  $O_2$ : 150 ml/min. Sample content:  $10 \mu\text{g Cl}^-$ .

The increasing blanks of sulfate concentration in the absorption solution do not permit the determination of organic sulfur in the  $\mu\text{g/l}$  level applying this active carbon for enrichment (Figure 6).

The adsorption of organic sulfur compounds has been performed using the sugar activated carbon (ZAK), which is produced by the Merck company.<sup>9,10</sup>



**Figure 6** Thermal desorption of HCl from TOX70 active carbon and sulfate blank formation. Conditions: See Figure 3.

### Conversion of sulfur organic compounds

The previous experiments have shown difficulties in determining sulfur organic compounds. A recovery of sulfate injecting diluted sulfuric acid into the quartz boat have not been estimated but the oxidation of the sulfur containing charcoal TOX70 has resulted in high blank values for sulfate. The behaviour of the bromine species, as pointed out, has been the same as observed with the sulfur species. Reaching blank values with low sulfate concentrations has been time consuming because the TOX70 active carbon with high sulfur content had been used in performing the pyrohydrolysis. This is caused by a rediffusion effect of S-species out of the quartz tube.

As described by several authors 0.10–0.30% hydrogen peroxide has been added to the absorption solution than have been adjusted to pH-values in the range 9–10.<sup>7,14</sup>

The pyrohydrolysis of stock solutions with concentrations of 200 mg/l S with respect to the organic compounds thiobenzamid or toluenesulfonic acid yield low recovery rates for low pyrohydrolysed volumes. The recovery rates have been increased up to 60–70% using higher volumes of model substance solutions. There has always been some sulfur left in the quartz tube, which effects increased blank values of sulfate.

Although using ionchromatographic determination of anions, the loss of sulfate cannot be explained, because no peaks for the sulfite anion in addition to the sulfate have been observed. For differentiation between  $\text{SO}_2$  and  $\text{SO}_3$  several experiments have been performed to determine the sulfur oxide which is absorbed from the absorption solution.

### Catalytic oxidation with platinum

For oxidation of sulfur dioxide in the reaction gases a platinum net is installed in the electric furnace. The recovery rates for sulfate obtained with thiobenzamid for changing temperatures is presented in Table 2. The nearly unchanged recovery at 1000 °C has indicated no activity of the platinum catalyst. For lower temperatures the activity is high and only sulfur trioxide is formed. But the resulting  $\text{SO}_3$  could not be absorbed from the absorption solution. These results are in agreement with the conditions of processing sulfuric acid. The optimum temperatures for catalyzing the oxidation of  $\text{SO}_2$

**Table 2** Influence of platinum catalyst to recovery of sulfate pyrohydrolysis of TBA

<i>Temperature</i> (°C)	<i>Recovery rate</i> (%)
1000	87 <sup>a</sup>
1000	91
800	1
700	0

<sup>a</sup>Without catalyst.

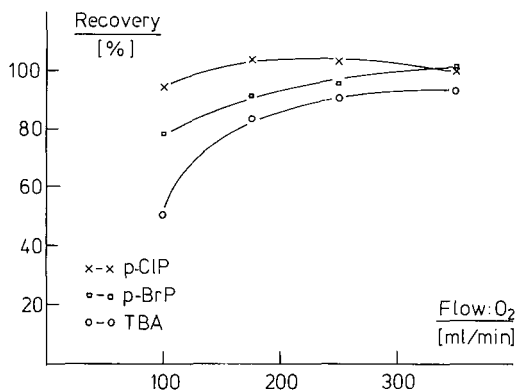
to SO<sub>3</sub> are in the range of 550–650 °C and the produced SO<sub>3</sub> cannot be absorbed in water. For absorption concentrated sulfuric acid is used.

Based on these results only the formed SO<sub>2</sub> by pyrohydrolysis is absorbed in contrast to formed SO<sub>3</sub>. This effect has been responsible for the loss of sulfate.

These results could be confirmed by an additional experiment. The absorber was filled with concentrated sulfuric acid to dry the reaction gases and to absorb the excess of sulfur oxides, when the TOX70 charcoal has been applied. A second absorber has been connected to the first absorber to collect the halogenides, as it is usual for AOX-determination.<sup>5,6</sup> No decreased values for sulfate concentrations have been observed which indicate the formation of SO<sub>2</sub>. The SO<sub>2</sub> could not be absorbed from the concentrated sulfuric acid.

### **Influence of oxygen flow rate**

Owing to the results an increase of the recovery of sulfate and bromide had to be achieved. The responsibility for the high blanks for both anions have been due to the diffusion of bromine and sulfur species into the heated quartz tube. Because the following desorption is observed, this desorption should be forced by applying higher oxygen flow rates during the analysis and the diffusion could be reduced simultaneously. The influence of oxygen flow on the recovery rates on the pyrohydrolysis of three model substances is demonstrated in Figure 7. A dependence of chloride absorption on the



**Figure 7** Influence of oxygen flow on recovery rates for conversion of model substances. Conditions: See Figure 3. Direct injection of stock solutions into the sample boat. Sample content: 10  $\mu\text{g}$  Cl<sub>2</sub>, Br<sub>2</sub>, S.

oxygen flow rate has been negligible, while the recovery rates for bromide have increased to the desired values. For sulfate also, a rising of recovery greater than 80% has been achieved, but an approach to values of 95% has remained desirable.

## CONCLUSIONS

With the first utilized pyrohydrolysis apparatus the desired recovery of sulfur and bromine compounds have not been approached. The reproducibility of recovery rates has been low, especially for sulfate formation. This behaviour may be due to the catalytic effects of observed visible depositions in the overpass from the high heated quartz tube to the absorption chamber (Figure 1).<sup>15,25</sup> A shorter time improvement of reproducibility has been achieved by renewal of the quartz tube. The increased temperature of the heating coil to 400 °C has produced better results too.

The maximum available temperature of the infrared heater has been decreased with longer utilization. Therefore decomposition with lower temperatures of the model substances could be contributed to the formation of higher SO<sub>3</sub> contents and therefore to a loss of sulfate.

The low recovery for conversion of sulfuric acid could be explained as follows: The decomposition of sulfuric acid has produced only  $\text{SO}_3$  in the first reaction step and the reaction time in the pyrohydrolysis apparatus has been too short for the reduction of the formed  $\text{SO}_3$  to  $\text{SO}_2$ .

The experimental investigations have pointed out several ways to increase the yields of sulfate formation.

Because only sulfur dioxide is absorbed, first the pyrohydrolysis conditions could be assimilated. The equilibrium for the exothermal reaction 1 can be shifted in direction of the  $\text{SO}_2$  formation with increasing temperature.<sup>10</sup>



Furthermore the always examined higher flow rates of oxygen can take positive influence for the yields of sulfate, based on lower reaction times in the cool zone, which the formed  $\text{SO}_2$  has to pass, before entering the absorption solution and oxidised to sulfate.

In addition to the above-mentioned effects the diffusion of bromine and sulfur species into the quartz tube should be reduced by decreasing the surface of the quartz assembly of the pyrohydrolysis apparatus. This dependence has not been inquired of in detail using it for developments of methods to determine low amounts of hetero atoms in organic compounds. But some reports in the numerous literature, describing methods for elementary analysis, show agreement with the found sources controlling especially the recovery for sulfur compounds.<sup>21-24</sup>

Based on these estimated results, following improvements on the pyrohydrolysis conditions and apparatus have performed (Figure 8). The infrared heater has been exchanged for a second electric furnace, which has been set movable on a rail. The drying of the sample in the quartz boat has been performed in the surrounding metal cylinder, which was heated to  $400^\circ\text{C}$ , resulting in a temperature of  $200^\circ\text{C}$  in the quartz tube. After drying for 3 min the furnace 1 has been moved to the left, oxidising the sample in 30–40 sec. For total sulfur species desorption out of the quartz tube the furnace is moved back after 15 min. After cooling the sample boat for 2 min, accompanied by heating the initially free part of the quartz capillary, the combustion is finished. The reaction time has increased from 15 to 20 min applying this procedure.

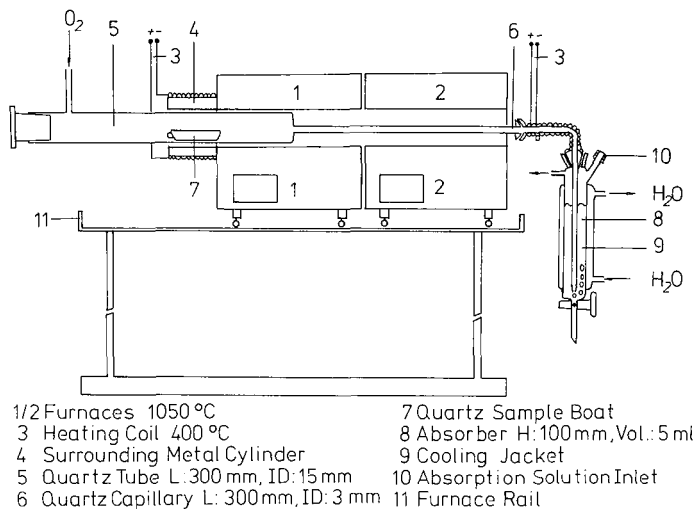


Figure 8 Modified pyrohydrolysis apparatus.

The absorption solution is pressed up into the capillary to rinse off condensed reaction products. The solution is then drained off, the absorber is rinsed with absorption solution and both filled up to 10 ml. Now 200  $\mu$ l of the solution is injected onto the ion-chromatographic column to separate and determine anion concentrations. Hydrogenperoxide solution (0.10%), adjusted to pH 9–9.5 has been used for absorption.<sup>10</sup>

The geometry of the quartz combustion has changed in order to obtain lower surfaces for the diffusion of the bromine and sulfur species (Figure 8). The quartz tube and the capillary in Figure 8 have a total surface of 10.7 cm<sup>2</sup> in comparison to the quartz tube including the connection to the absorber in Figure 1 which have a surface of 20.7 cm<sup>2</sup>. The connection from the quartz assembly of the high heated zone to the absorption solution has been reduced from 8.3 cm<sup>2</sup> to 1.9 cm<sup>2</sup>.

The temperature for combustion of the adsorbates has been increased from 950 °C to 1050 °C providing a theoretical yield of 95% SO<sub>2</sub>.<sup>10</sup>

An oxygen flow for pyrohydrolysis of 300 ml/min has been used. With the described improvements on the pyrohydrolysis apparatus and changed combustion conditions better results have been

achieved. The blanks for sulfate have decreased. The recovery rates for sulfate in addition to bromide and chloride could be increased to values above 93%.

The obtained results for the calibration of the analysis method including the enrichment of the model substances using sugar active charcoal and a list for the recovery rates of nearly sixty organic compounds containing chlorine, bromine, or sulfur are described in another report.<sup>10</sup>

### Acknowledgements

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