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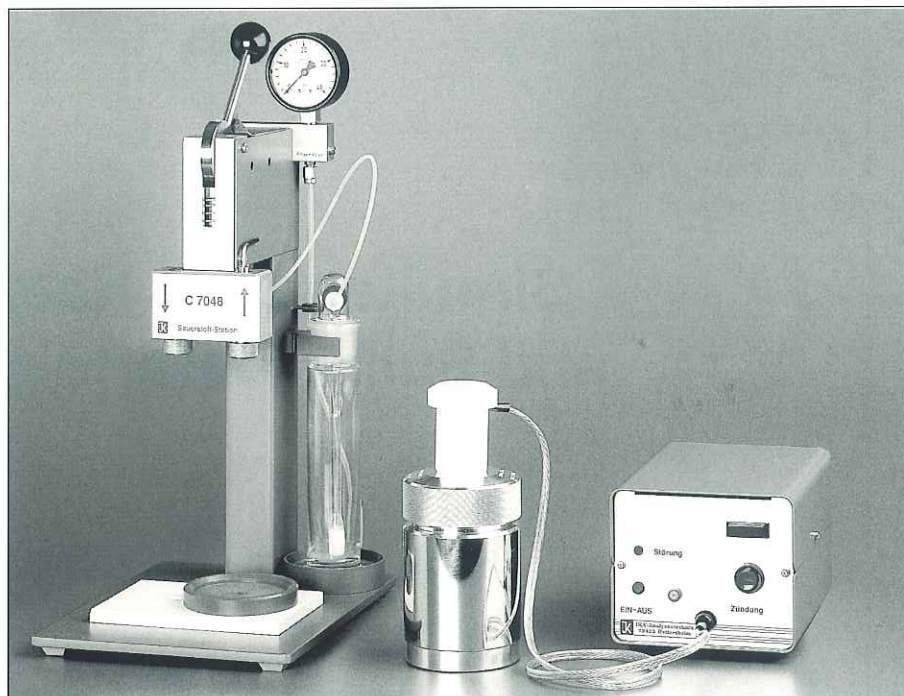
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HANS ALBRICH AND MICHAEL MÜLLER*

Simultaneous Halogen- and Sulfur Determination

After a combustion decomposition in a calorimeter bomb

A simultaneous determination of fluorine, chlorine, bromine, iodine and sulfur contents can be carried out with high reproducibility, with retrieval rates of almost 100 % and with short decomposition times after a combustion decomposition in a decomposition bomb. After the quantitative absorption of ionogenic combustion products in an aqueous medium, joined by an ionchromatographic separation, detection limits below 10 ppm are easily obtained.



III. 1: AOD Decomposition System

Since the second general Administration of Refuse Act (TA-Abfall) [1] has been published, an increased interest in a cost-saving and rapid procedure for a simultaneous halogen- und sulfur determination [2-4] has been expressed in a series of publications. Thus many refuse disposers and operators of combustion plants demand, beside the determination of chlorine, sulfur and the calorific value, also routinely a determination of the parameters fluorine, bromine and iodine. At the same time experts resumed their discussion about a procedure for an element-specific AOX-determination [5]. In order to make allowances for this development, working groups have lately

been endeavoured to find a uniform procedure for a simultaneous determination of halogen and sulfur contents [2-4].

The basic principle of most of the suggested procedures was an oxidative combustion decomposition joined by an absorption of the combustion products in an aqueous medium. Detection and quantification of the relevant analysed substances is then carried out in this absorption solution. In this field the ionchromatography is doubtless the determination procedure of choice. Especially if the samples to be investigated contain apart from chlorine and sulfur also halogens such as fluorine, bromine and mainly iodine, there is no real alternative for the ion-chromatographic determination procedure, as already described in DIN 38414 part 18 (Deter-

mination of AOX in sludges and sediments) [6]. The substances to be analyzed, however, should have a uniform ionogenic form (X^- ; SO_4^{2-}). During the combustion of materials containing halogen and sulfur, apart from HX and SO_2 , also further ionic and non-ionic species (table 1) can form in different concentrations.

It was the aim of this work to develop – following already existing DIN resp. EU-standards – a procedure that considers the described problems already from the start. Main focus was the combustion decomposition itself. We wanted to find a decomposition technique that excludes right from the beginning and as far as possible the formation of SO_2 , X_2 , XY and oxihalogen respectively. This should also essentially simplify the finding of a universal absorption solution.

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Decomposition and Absorption

Basically, several decomposition methods are suitable for the simultaneous determination of halogen and sulfur [7-9]. Compared with marketable procedures such as the Wickbold method or combustions in a quartz tube according to Grote-Kreker, a bomb decomposition acc. to DIN 51577-A offers some marked advantages.

Firstly, weighed samples up to 1 g are possible, which is making allowances for the inhomogeneity of many real samples. Secondly, detection limits below 10 ppm can be obtained when using the ion chromatographic procedure of determination, and that with absorption volumes between 10 and 20 ml (Wickbold decompositions require 200 ml). And thirdly it is the procedure that meets all requirements for a total sample decomposition and the quantitative absorption of all analysed substances (table 2). Liquid, liquid-pasteous and solid samples can be processed.

As conventional calorimeter bombs were not sufficiently anti-corrosive, and as the resulting absorption solutions because of their partly very high heavy metal contents (Fe, Cr and Ni > 1000 ppm) were practically unusable for a joining anionic separation by means of an ion chromatograph, this procedure is less known so far.

With the here used decomposition system AOD of Messrs. IKA-Analysentechnik, consisting of decomposition vessel, oxygen filling and ventilating station, cooling vessel and remote ignition device (photo 1), the analyst has for the first time an instrument at his disposal that includes all advantages of bomb decomposition.



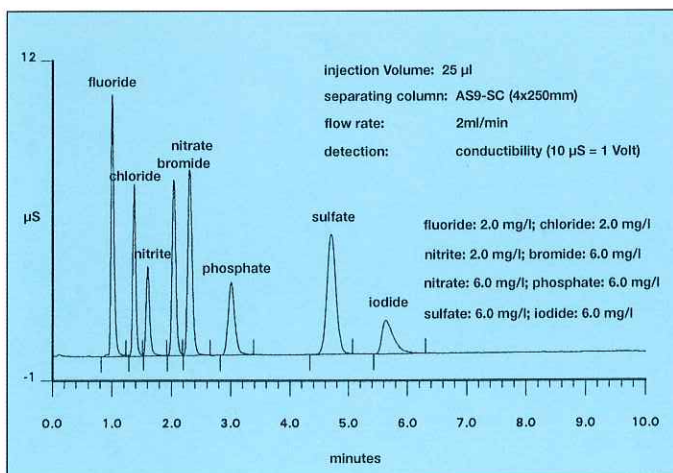
III. 2: Decomposition vessel for AOD and/or C 7000

Educts	Products
organohalogenic-compounds	hydrogen halides (HX) molecular halides (X ₂) inter halide compounds (XY _n) halogen oxide acids (HXO _n)
organic sulfur compounds	sulfur dioxide (SO ₂) sulfur trioxide (SO ₃)

Table 1: Possible combustion products by an oxidative decomposition of materials containing halogen and sulfur.

Bomb decomposition	Advantages
sealed system (V = const)	complete combustion
high oxygen particle pressure (30 bar)	no analytic loss (quantitative absorption)
optimum temperature conditions (core temperature appr 1250 °C)	complete oxydation from "S" over SO ₂ to SO ₃
ambient temperatures < 400 °C	suppression of the X ₂ XY- and oxyhalogenide formation
catalytically active metal surface	increased solubility of the combustion products

Table 2: Requirements for a complete sample decomposition and for a quantitative absorption of all analyzed substances are met by the basic principles of bomb decomposition.



III. 3: Ionchromatogram of an aqueous mixing standard

The core of the AOD-system is the decomposition vessel (photo 2). Special alloys that are resistant even under extreme chemical and physical conditions, create optimal pressuppositions for a "bomb decomposition". Decomposition vessels and/or colorimeter bombs are also available in an additionally catalytic activated form.

Performing Decompositions

Decompositions were carried out following DIN 51577-A [9] standards. Shortly before the combustion, the homogenized samples were transferred to acetobutyrate capsules serving as a

combustion aid at the same time. These capsules were put into the combustion crucibles made of quartz glass and were fixed to the electrodes. The weighed real samples varied, depending on the halogen and/or sulfur contents, from just a few (generally 100–200 mg) up to 1.0 g.

A decomposition of low-caloric samples and of powdery solid samples respectively requires additional combustion aids (benzoic acid or paraffin). In this case, principally a layer of 100–200 µm paraffin perliquidum is put on the samples in the acetobutyrate capsules. If combustion aids are used, they have to be considered in the blind value measure-

Table 3: Used reference materials and model substances

Reference materials		Element contents in weighed %				
Name	No.	fluorine	chlorine	bromine	iodine	sulfur
Thiourea	1	-	-	-	-	42.13
L-Cystein	2	-	-	-	-	26.47
2, 4, 6-Trichlorophenole	3	-	53.87	-	-	-
3-Chloro-4-Fluoroaniline	4	13.05	24.36	-	-	-
Bromothymol Blue	5	-	-	25.59	-	5.14
2-Iodineaniline	6	-	-	-	57.94	-
o-Iodinehippur acid	7	-	-	-	41.60	-
N-(2-Chloro-4-nitrophenyl)-N'-(4-iodophenyl)-thiourea	BCR 72	-	8.11	-	29.32	7.35
1-[1-(4-Bromophenylmethyl)-4-piperidinyl]-5-chloro-2-(trifluoromethyl)-1H-benzimidazol	BCR 73	12.07	7.49	16.90	-	-

Table 4: Medium retrieval and repeatability variation coefficients after N combustions with different weighed samples.

Samples	N	fluorine		chlorine		bromine		iodine		sulfur	
		WF [%]	VK [%]	WF [%]	VK [%]	WF [%]	VK [%]	WF [%]	VK [%]	WF [%]	VK [%]
1	10	-	-	-	-	-	-	-	-	98.5	1.7
2	10	-	-	-	-	-	-	-	-	100	1.9
3	10	-	-	99.6	2.4	-	-	-	-	-	-
4	10	97.8	3.2	101	2.3	-	-	-	-	-	-
5	10	-	-	-	-	98.4	4.0	-	-	97.6	3.2
6	10	-	-	-	-	-	-	99.2	4.1	-	-
7	10	-	-	-	-	-	-	102	3.6	-	-
4/5	15	99.2	2.9	98.7	1.9	98.6	3.5	-	-	98.9	2.1
4/5/6	15 ^a	101	2.3	99.2	2.0	99.5	3.2	92.6	4.2	101	2.3
	5 ^b	99.8	2.4	101	1.7	99.7	3.6	96.5	3.9	99.6	1.9
BCR 72	10	-	-	100	2.7	-	-	98.2	3.8	102	2.9
BCR 73	10	98.9	2.7	102	2.6	101	3.7	-	-	-	-
BCR 72/73	15 ^a	102	2.5	99.5	1.9	99.8	3.5	89.4	5.1	99.7	2.8
	10 ^b	101	2.8	101	2.1	98.9	3.6	95.7	4.3	100	2.6
sample of waste oil with 2.86 ± 0.098 g chlorine/kg and 7.88 ± 0.14 g sulfur/kg											
sample of waste oil + BCR	5 ^b	99.8	2.6	99.6	1.7	100	3.9	96.3	4.3	99.8	2.7

a) combustion in a non-activated bomb

b) combustion in a bomb with catalytically activated surface

ment. For ignition, special ignition wires are fixed to the electrodes. Ignition wires have to be long enough to touch the acetobutyrate capsules. Occasionally it is of advantage, however, to use shorter wires having been processed into benzoic acid

pressings. Because of the blind value problem, no cotton wool threads should be used.

Before the combustions, precisely 10 ml diluted sodium hydroxide and, depending on the element contents to be

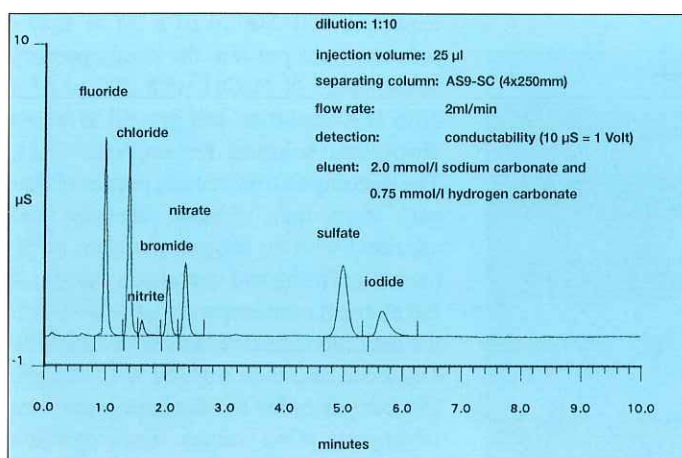
expected, 100–500 µl of a 30 % H₂O₂-solution were put into the decomposition vessel (0.25 N NaOH with 200 µl of a 30% H₂O₂-solution has proved to be an absorption solution for universal use). The decomposition vessels prepared that way were then closed carefully and admitted with an oxygen pressure of 30 bar at the filling and expansion station. If the element contents were very low, then the decomposition vessels were carefully expanded and then refilled with oxygen (30 bar) in order to eliminate/minimize laboratory blind values. Each ignition was carried out by means of the remote ignition device in a safety containment scheduled for this purpose.

Alternately, the ignition can also be carried out in the calorimeter C 7000 [3]. In this case a fully automatic calculation of the calorific value according to DIN 51900, ISO 1928, ASTM 240 D standards etc. is possible. Depending on the combustion behaviour of the individual samples, the decomposition vessels cooled down after the combustion within five to ten minutes.

After a slight agitation, the combustion gases were expanded at the expansion station via a gas washing bottle, and the decomposition vessels were opened. The absorption solutions were filled by weighing in bidistilled water up to a defined volume (e.g. 100 ml is 89.5 g H₂O). A joining filtration (cellulose acetate filter, pore size 0.45 µm) supplied the finished measuring solutions. If required, these were further diluted with ionchromatographic elution buffers.

Ionchromatographic Separation and Evaluation

In the filtered absorption solutions, existing halogenides and sulfations could be ion-chromatographically determined according to DIN 38405, part 19 [10]. In the application described here, the ionchromatograph DX-100 with membrane suppressor and conductivity detector of Messr. Dionex was used. For the isocratic separation of the anions, the anion exchange columns IonPac AS4A-SC (4x250 mm) and IonPac AS9-SC (4x250 mm) in conjunction with corresponding precolumns AG 4 and AG 9 respectively were used (ill. 4). The advantages of the AS9-SC-column com-

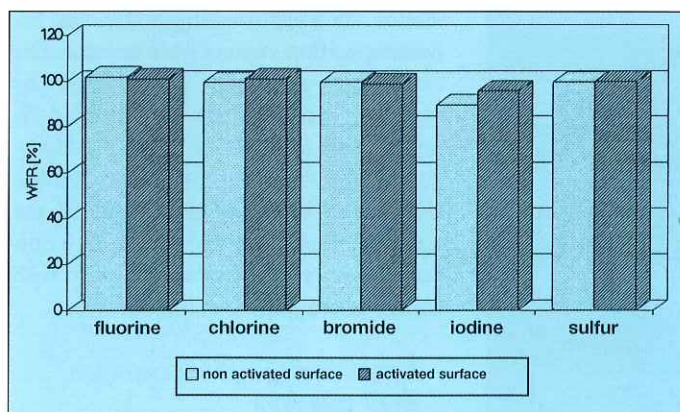


III. 4: Ionchromatogram after a decomposition of 9.8 mg BCR 72 and 10.1 mg BCR 73.

pared with the AS4A-SC column are that polarizable anions elutriate relatively early in it, and thus the determination of iodide is made possible. Furthermore, oxihalogenids can be separated with it, whose detection indicates possible "reduced halogen findings". If no iodine determination is required, the less pH-dependent AS4A-column should be preferred.

For measurement served a standard calibration procedure with marketable

and BCR 73) of the Community Bureau of Reference-BCR were used. As can be seen from table 3, these reference materials include fluorine, chlorine, bromine and iodine as well as sulfur. These solid materials were decomposed and examined according to the procedure described before, either individually or as a defined compound of several model substances. The weighed samples varied between 10 and 100 mg per model substance. For smaller weighed samples



III. 5: Graphic image of retrieval rates after combustion of multi-element-standards BCR 72/73 in bomb with and without a catalytically activated surface.

anion standards (ill. 3). The automatic peak surface evaluation with the help of the chromatographic software AI 450 supplied the halogenide and/or sulfate concentrations of the respective measuring solution in mg/l. After a corresponding blind value correction, the absolute and/or element contents in relation to the weighed samples could be calculated.

Precision and Retrieval Rates

For checking the overall procedure, several model substances were used. Thus also certified standards (BCR 72

and/or for increasing real samples, standard solutions in DMF were used.

Results and Discussion

The results obtained according to the procedure described here are compiled in table 4 (see also ill. 5). The individual elements could be determined, independent of their concentration, with a retrieval rate of almost 100 % and with a very good reproducibility. In the iodine determination, a few minor cross sensitivities could be observed. The retrieval rates here were also higher than 98%, but

only in a combustion of bromine-free model substances such as iodaniline or BCR 72 (table 4). In bromine containing multi-element-standards, however, iodine could "only" be determined with reduced findings of up to 10 %, whereby decompositions in bombs with additionally catalytically activated surfaces supplied clearly better results with retrieval rates of more than 95 %. Possibly the formation of iodobromine is one of the reasons for these "reduced findings". Normally IBr, one of the easier accessible interhalogen compounds of type XY, disproportionates in water to bromide and hypoiodide. Under the conditions given here, hypoiodide should further disproportionate to iodide and iodate [11]. In the obtained absorption solutions, however, neither hypoiodide nor iodate could be detected. And more so, occasionally slightly yellow colored decomposition solutions (with further evidence by KI-starch paper) indicated the existence of small traces of elementary iodine. This fact could strictly formally be explained by the mechanism shown in equation 1. This hypothesis is supported by the quantitative assessment of bromide contents after combustion with compounds containing iodine (table 4).



The determination of the fluorine, chlorine, bromine and sulfur contents presented no problems, neither after combustions in decomposition vessels with nor in those without an additionally activated surface. No concentration or matrix dependencies were noted. These facts, and mainly the high retrieval rates in sulfur content determinations can only be explained by the optimal decomposition conditions (table 2) in the calorimeter bomb.

Thus also in H₂O₂-free absorption solutions no sulfite could be detected by way of an ion-chromatograph, which indicates a quantitative oxydation of the first formed SO₂ to SO₃ in the gaseous phase already.

Conclusion:

By a combustion decomposition in the calorimeter bomb of the decomposition system AOD, samples containing halo-

gen and sulfur can be decomposed rapidly and without problems. It could be shown that fluorine, chlorine, bromine, iodine and sulfur contents are quantitatively assessed after absorption and ionchromatographic determination. The overall procedure introduced here excels in:

- easy and safe handling with minimal instrument requirements
- short decomposition times
- high precision and very good reproducibility
- retrieval rates between 95 % and 105 %
- low cross sensitivities and
- detection rates in the low ppm-range.

Thus, this procedure meets all requirements for an element-specific AOX-, EOX- and AOS-determination, and should establish itself in future as current method for this area.

Furthermore, the decomposition for the joining heavy metal determination (Hg, Cd) is thinkable whereby a combustion in the C7000 up to the flash point, all combustion parameters would be accessible.

Acknowledgement:

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