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Note

Determination of heteroatoms in organic compounds by ion chromatography after Schöniger flask decomposition*

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The Schöniger flask combustion technique is a very useful method for decomposing organic matter[1]. In our laboratory it has been used, in conjunction with titrimetry, for determination of the halogen, phosphorus and sulphur contents of organic materials. During the combustion and the trapping process, the halogens are converted to the halides, phosphorus and sulphur are oxidized to phosphate and sulphate, and are subsequently determined as such.

Ion chromatography (IC) is a powerful technique for the sequential determination of anions. Initial work using the suppressor mode with carbonate/bicarbonate eluent has indicated its usefulness when employed with the Schöniger flask decomposition[2,3]. This report describes our experience, with emphasis on comparison with titrimetry, in using the non-suppressed, single column mode with the Schöniger decomposition.

EXPERIMENTAL

The apparatus for ion chromatography consisted of a dual-piston reciprocating pump (Waters, Model 6000A), a loop injector (Rheodyne, Model 7125), a small particle diameter, silica based column for anion separation (Vydac 302 IC), a precolumn of similar material, an ultraviolet detector (Waters, Model 450) and a conductivity detector (LDC, Model 701) connected in series.

The effluent was 0.002 *M* phthalic acid adjusted to pH values ranging from 3.5 to 5.5 with sodium tetraborate. The usual flow-rate was 1 ml/min and most injections were made with a 20-μl sample loop.

For Schöniger flask decomposition, an accurately weighed sample (*ca.* 30–50 mg) was wrapped in a piece of carrier paper, mounted on the platinum holder and combusted in the usual manner. Two absorber solutions: (1) 6% hydrogen peroxide in 0.18 *M* sodium hydroxide, and (2) 2% hydrazine sulphate in distilled deionized water, were used routinely. The absorber solution was diluted to 50 ml with water after combustion.

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TABLE I

TYPICAL ACCURACIES

X = Heteroatoms. A = *p*-dichlorobenzene, B = α,α′-dibromo-*p*-xylene, C = sulphosalicylic acid, D = combination sample of the three compounds.

Standards	*ppm X expected*	*ppm X found*	*Rel. error (%)*
A	34.6	35.2	1.7
B	31.8	312.3	1.6
C	7.99	7.47	6.5
D-Cl^-	11.3	10.3	8.8
D-Br^-	13.1	13.0	0.8
D-SO_4^{2-}	9.01	8.62	4.3

RESULTS AND DISCUSSION

There is much discussion in the literature as to the best absorber solution for Schöniger flask decomposition[4,5]. We find both the hydrogen peroxide and the hydrazine sulphate solutions adequate. The latter is often preferred when titrimetry is to be used after decomposition[4]. For IC determination, the hydrazine sulphate solution is less desirable as it contains a high concentration of sulphate, which not only makes sulphate determination impossible but also overloads the column. The hydrogen peroxide solution is preferred since it does not contain any interfering ions or cause column overloading.

The accuracy and speed of the IC determination are demonstrated in the analysis of some standards: *p*-dichlorobenzene, α,α′-dibromo-*p*-xylene and sulphosalicylic acid. The results are shown in Table I. The accuracy obtained (1–9%) is typical. The total analysis time for the three anions determined in a single run is *ca.* 15 min, which is considerably shorter than that required for three determinations in titrimetry (*ca.* 70 min). In addition, IC requires virtually no operator interaction once the sample has been injected and frees the analyst to perform other tasks between injections. Another point of practical importance is that each IC run requires only a minute portion of the decomposed sample (normally about 20 μl) whereas titrimetry often consumes the whole sample. Thus IC allows replicate analyses of one burn while titrimetry does not. Table II shows the results of several chloride analyses performed both by IC and titrimetry. Agreement between the two is good.

TABLE II

CHLORIDE ANALYSIS

Sample	*ppm Cl^-*	
	IC	*Titrimetry*
E	35.3	38.3
F	11.7	11.7
G	15.1	15.8

TABLE III

DETECTION LIMITS

Detection limits are expressed as amounts in the original sample.

Heteroatom	*IC (ng)**	*Titrimetry (ng)*
Cl	0.1	0.7**
Br	0.1	1.6**
S	0.1	0.5***

* UV detection.
** Silver nitrate titration.
*** Turbidimetry.

The detection limits for both IC and titrimetry are estimated in Table III. IC is certainly a more sensitive technique than titrimetry. Further, with on-column preconcentration, the sensitivity of IC may readily be enhanced ten-fold or more. In general, the precision of titrimetry (*ca.* 1%) is considerably better than that of IC (*ca.* 5%). However, the superior precision of titrimetry is not necessarily realized when used in conjunction with the Schöniger flask decomposition as error larger than 1% can easily be introduced in the combustion process.

In summary, ion chromatography is an accurate, rapid and sensitive method for heteroatom analysis after the Schöniger flask decomposition.

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