

Determination of Halogen Elements in Volatile Organohalogen Compounds by the Wickbold Combustion Pretreatment Method and Ion Chromatography

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A quantitative analysis method of halogen elements in volatile organohalogen compounds was established by the Wickbold combustion pretreatment in an enclosed system and ion chromatography. The sample pretreatment parameters of Wickbold combustion were experimentally optimized, and using the determined optimal pretreatment parameters, the reproducibility was estimated by ion chromatography. As a comparison for real samples, NIST certified reference materials (CRMs) were analyzed for the recovery efficiency and reproducibility.

Key Words : Halogen element, Wickbold combustion, Organohalogen compound

Introduction

Organohalogen compounds are used as surface coating reagents, flame retardants, fire-proofing agents, and insecticides in various polymer and fine chemical fields. Although many analysis methods¹⁻¹² of halogen elements in organohalogen compounds have been studied for a long time, it is very difficult to quantitatively determine the amount of halogen elements because of their volatile nature.

In this study, halogen elements in organohalogen compounds were pretreated by the Wickbold combustion apparatus and analyzed by ion chromatography to prevent their volatile problem. The Wickbold combustion method¹³⁻²² for decomposition has been known for almost 50 years. It was developed for the analysis of sulfur and nitrogen in organic samples, particularly in petroleum and mineral oil. Since then the apparatus has been modified several times and it has also been applied to the analysis of volatile metals such as arsenic, antimony, and selenium. Because the Wickbold combustion apparatus is made of quartz, samples can be burned at more than 2,000 °C in an oxyhydrogen flame without contamination occurring. Furthermore, all samples can be pretreated in an enclosed system without loss of volatile elements.

As shown in Figure 1, the Wickbold combustion apparatus consists of a shell oven, a solid state burner, a burning chamber, a cooling device, an absorption tube, a solution tank, a rinsing device, and a flask for decomposition solution. For complete combustion, samples are changed to gaseous state at 700-1,000 °C in the shell oven; then the gas is vacuum-pumped at 500 mbar to the combustion chamber and burned completely by the 2,000-2,500 °C oxyhydrogen flame in the burning chamber. During this procedure, all carbon-halogen bonds are broken, then CO₂ and hydrogen halogenide (HX) are simultaneously formed. The CO₂ and HXs go through the cooling condenser with water vapor, which is produced from the oxygen-hydrogen reaction. In the absorption tube, hydrogen halogenide ions are absorbed

into alkali absorption solution, which is then analyzed quantitatively by ion chromatography.

Experimental Section

Apparatus. A Wickbold combustion apparatus (V5, Heraeus Quarzglas GmbH, Germany) (Figure 1) was used for sample pretreatment. An ion chromatograph (DX-300, Dionex, USA) was used to determine halogen anion content in the digested sample solutions after the Wickbold combustion step.

Materials. The certified halogen anion standards (each 1,000 ppm solution) were obtained from Alltech. Distilled water was purified by Milli-Q plus (Millipore Co.) and the solutions were filtered through a 0.45 μm membrane filter and degassed. All authentic reagents (>99%) used to test the optimal parameters were obtained from Merck. NIST (National

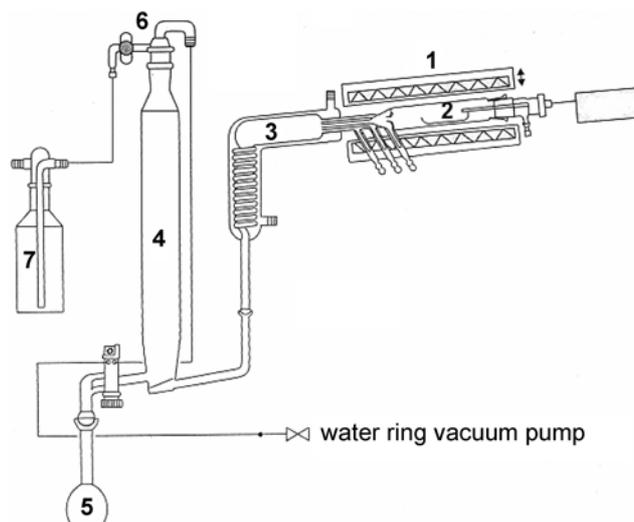


Figure 1. The Wickbold combustion apparatus V5 : (1) shell oven, (2) solid state burner (3) burning chamber and cooling condenser (length:30 cm), (4) absorption tube (5) flask for decomposition solution, (6) rinsing device, (7) solution tank

Institute of Standards and Technology, Gaithersburg, MD, USA) SRM 1630a, 2695, 2142, 2143, and 2144 were used as CRMs. Oxygen, hydrogen, and nitrogen were used for the Wickbold combustion at flow rates of 18 L/min, 8 L/min, and 1.5 L/min, respectively. The purity of gases was 99.999%.

Determination of optimal parameters of Wickbold combustion. For the optimization of the Wickbold combustion pretreatment procedures, the recovery rate of halogen elements was determined by ion chromatography in relation to pyrolysis temperature, concentration of absorption solution and sample weight in the Wickbold combustion pretreatment. 5-Fluoro-2-methylaniline (F 15.18 wt%), and 1-bromo-4-nitrobenzene (Br 39.55 wt%) were used as authentic reagents of fluorine and bromine, respectively.

Pyrolysis temperature: Pyrolysis involved two steps. The first step raised the temperature of the sample to 700-900 °C in the shell oven. The second step raised the temperature of the sample to 800-1,000 °C with O₂ in the shell oven. Then all gaseous compounds were burned completely at 2,000-2,500 °C by an oxyhydrogen flame in the burning chamber. This test was carried out on 0.10 g of sample and 0.1 mol/L NaOH absorption solution.

Concentration of absorption solution: After the second pyrolysis, hydrogen halogenides were absorbed into alkali absorption solution in ionic form after going through a cooling condenser with water vapor. The concentrations of absorption solution were measured between 0 and 0.2 mol/L NaOH. This test was carried out on 0.10 g of sample with pyrolysis temperatures of 800 °C and 1,000 (1st step and 2nd step, respectively).

Sample weight: Sample weight was tested between 0.10 g and 5.0 g. This test was carried out under pyrolysis temperatures of 800 °C and 1,000 (1st step and 2nd step, respectively) with 0.1 mol/L NaOH absorption solution.

Ion chromatography analysis. An IonPac AS9-SC analytical column (Dionex, USA), an IonPac AG9-SC guard column (Dionex, USA), and a conductivity detector were used. The eluent consisted of a mixture of 1.8 mM Na₂CO₃ and 1.7 mM NaHCO₃. The flow rate was 1.0 mL/min and the injection volume was 100 μL. Alkali absorption solution obtained from the sample pretreatment by Wickbold combustion was diluted with distilled water to 100 mL in a volumetric flask. Five-point (0, 2, 10, 50, 100 ppm) calibration curves of each halogen element were created using the

halogen anion standard solutions. The diluted alkali absorption solution was then submitted to ion chromatography and the halogen element concentration of the absorption solution was determined using the standard curves. If the halogen element concentration of the absorption solution was above the calibration range, then it was diluted appropriately to a concentration within that range.

Reproducibility and limit of detection. Using the previously determined optimal conditions of the Wickbold combustion method, the reproducibility (n = 7) was estimated by ion chromatography. 5-Fluoro-2-methylaniline (F 15.18 wt%), 9-Fluorenylmethyl chloroformate (Cl 13.70 wt%), and 1-Bromo-4-nitrobenzene (Br 39.55 wt%) were used as authentic reagents of fluorine, chlorine, and bromine, respectively.

The limit of detection (LOD) and the limit of quantitation (LOQ) were estimated by ion chromatography following the Wickbold combustion pretreatment procedures. The average of blank values and the standard deviation were measured by a blank test and a standard curve.

Analysis of the certified reference materials. NIST SRM 1630a, 2695, 2142, 2143, and 2144 were used as CRMs for the recovery efficiency and reproducibility. According to the optimal parameters of the Wickbold combustion pretreatment, 1.00 g each of SRM 1630a and 2695 was used, and 0.10 g each of SRM 2142, 2143, and 2144 was used.

Results and Discussion

Determination of optimal conditions of Wickbold combustion. The various experiments of pyrolysis temperature (Table 1) showed that the recovery was over 94% at 800 °C/900 °C (1st step and 2nd step). Also the result at 700 °C/1000 °C showed a good recovery as one of 800 °C/900 °C. If there is not a strong sparking between oxygen and indecomposable sample in the burning chamber, the first pyrolysis temperature is not important. Additionally, if the second pyrolysis temperature is 1,000 °C, good recovery results are expected.

In the experiment of the concentration of absorption solution (Table 2), the recovery of over 95% was determined with all concentrations over 0.01 mol/L NaOH except no addition of NaOH.

Table 1. The recoveries by the various temperatures of pyrolysis (1st/2nd)

Temperature Condition (°C) (1 st /2 nd)	Recovery					
	F			Br		
	Theory (wt%)	Measured (wt%, n = 5)	Recovery (%)	Theory (wt%)	Measured (wt%, n = 5)	Recovery (%)
700/800		13.63 ± 1.46	89.79		32.04 ± 0.98	81.01
700/900		14.26 ± 0.59	93.94		37.70 ± 0.84	95.32
700/1,000	15.18	14.89 ± 0.35	98.09	39.55	38.63 ± 0.60	97.67
800/900		14.32 ± 0.62	94.33		37.58 ± 0.66	95.02
800/1,000		15.05 ± 0.29	99.14		39.09 ± 0.61	98.84
900/1,000		15.01 ± 0.21	98.88		39.12 ± 0.73	98.91

Table 2. The recoveries by the various concentrations of absorption solution

Concentration (mol/L NaOH)	Recovery					
	F			Br		
	Theory (wt%)	Measured (wt%, n = 5)	Recovery (%)	Theory (wt%)	Measured (wt%, n = 5)	Recovery (%)
0		14.03 ± 0.73	92.42		37.31 ± 0.92	94.34
0.01		14.46 ± 0.36	95.26		38.53 ± 0.61	97.42
0.05		14.99 ± 0.51	98.75		38.96 ± 0.50	98.51
0.075	15.18	14.89 ± 0.48	98.09	39.55	38.77 ± 0.43	98.02
0.1		15.12 ± 0.30	99.60		39.24 ± 0.52	99.22
0.15		14.95 ± 0.55	98.48		39.19 ± 0.79	99.09
0.2		15.07 ± 0.41	99.28		39.08 ± 0.42	98.81

Table 3. The recoveries by the variation of sample weight

Sample Weight (g)	Recovery					
	F			Br		
	Theory (wt%)	Measured (wt%, n = 5)	Recovery (%)	Theory (wt%)	Measured (wt%, n = 5)	Recovery (%)
0.10		15.35 ± 0.46	101.12		39.12 ± 0.26	98.91
0.50		14.97 ± 0.29	98.62		39.18 ± 0.55	99.06
1.00	15.18	15.04 ± 0.41	99.08	39.55	39.62 ± 0.49	100.18
3.00		14.48 ± 0.79	95.39		38.10 ± 1.10	96.33
5.00 ^a		not available			not available	

^aNot available with >5 g sample because of serious sparks at around 400 °C.

Table 4. Result of reproducibility test

Test Result (n = 7)	Contents of halogen element (wt%)		
	F	Cl	Br
Mean value	15.02	13.24	38.91
σ (S.D.)	0.28	0.41	0.52
Theory	15.18	13.70	39.55

Table 5. Limit of detection (LOD) and limit of quantitation (LOQ)

	Halogen elements (ppm)		
	F	Cl	Br
LOD (3 σ)	0.093	0.14	0.11
LOQ (10 σ)	0.31	0.48	0.36

Also, the results of the sample weights testing (Table 3) demonstrated that there is no significant difference between sample weights of 0.10 g and 3.00 g, however, 5.00 g of sample produces a lot of fumes at around 350 °C and sparks at around 400 °C, which interrupted the experiment.

Table 6. The recovery efficiencies of the certificated reference materials

Materials	Element	Certified Value (wt%)	Measured Value (wt%, n = 5)	Recovery (%)
NIST SRM 1630a (Traces in Coal)	Cl	0.1144 ± 0.0032	0.1097 ± 0.0076	95.89
NIST SRM 2695 (Fluoride in Vegetation)	F	0.0277 ± 0.0027	0.0269 ± 0.0032	97.11
NIST SRM 2142 (<i>o</i> -Bromobenzoic Acid)	Br	39.80 ± 0.05	39.88 ± 1.17	100.2
NIST SRM 2143 (<i>p</i> -Fluorobenzoic Acid)	F	13.54 ± 0.01	13.37 ± 0.46	98.74
NIST SRM 2144 (<i>m</i> -Chlorobenzoic Acid)	Cl	22.62 ± 0.05	22.05 ± 0.67	97.48

Per the results, the optimal conditions of the Wickbold combustion pretreatment were as follows: pyrolysis temperature of 800 °C/1,000 °C (1st step/2nd step), absorption solution of 0.10 mol/L NaOH, and 0.10-1.0 g of sample.

Reproducibility and limit of detection. The results (Table 4) showed both reproducibility and low standard deviation.

The average of blank values (n = 10), and the LOD and LOQ were measured (Table 5). LOD and LOQ values were represented as 3 σ and 10 σ , respectively.

Analysis of certificated reference materials. The recovery efficiencies (Table 6) by the optimized Wickbold combustion pretreatment and ion chromatography were over 95%.

Conclusion

In this study, a quantitative analysis method of halogen elements in volatile organohalogen compounds was established using the optimized Wickbold combustion pretreatment and ion chromatography. The quantitative analysis

performed using this method is effective because a lot of organic matrix and inorganic salts were eliminated during combustion pretreatment. The pretreatment by the Wickbold combustion apparatus makes it possible to burn organic compounds completely in an enclosed system, which can prevent unwanted contamination and loss of volatile halogen elements. The total analysis time was about 50 minutes per sample, which is significantly reduced compared to other methods. Therefore, this quantitative analysis method using the optimized Wickbold combustion pretreatment and ion chromatography, which provides good reproducibility and good recovery, is recommended for the determination of halogen elements in organohalogen compounds.

References

1. Cheng, F. W. *Microchemical Journal* **1959**, 3, 537.
 2. Fildes, J. E.; Macdonald, A. M. G. *Analytica Chimica Acta* **1961**, 24, 121.
 3. Kirsten, W. J. *Microchemical Journal* **1963**, 7, 34.
 4. Ota, S. *Japan Analyst* **1966**, 15, 689.
 5. Ota, S. *Japan Analyst* **1969**, 18, 1257.
 6. Hozumi, K.; Tamura, H. *Microchemical Journal* **1969**, 14, 47.
 7. Pecherer, B.; Gambrell, C. M.; Wilcox, G. W. *Anal. Chem.* **1950**, 22, 311.
 8. Singer, L.; Armstrong, W. D. *Anal. Chem.* **1959**, 31, 105.
 9. Venkateswarlu, P. *J. Dent. Res.* **1990**, 69, 514.
 10. Venkateswarlu, P. *Anal. Chem.* **1982**, 54, 1132.
 11. Jones, B. C.; Heveran, J. E.; Senkowski, B. Z. *J. Pharm. Sci.* **1971**, 60, 1036.
 12. Liggett, L. M. *Anal. Chem.* **1954**, 26, 748.
 13. Wickbold, R. *Angew. Chem.* **1952**, 64, 133.
 14. Wickbold, R. *Angew. Chem.* **1954**, 66, 173.
 15. Friese, H. *J. Mikrochim. Acta* **1981**, I(3-4), 265.
 16. Hoppstock, K.; Michulitz, M. *Analytica Chimica Acta* **1997**, 350, 135.
 17. Sweetser, P. B. *Anal. Chem.* **1956**, 28, 1766.
 18. Erber, D.; Quick, L.; Roth, J.; Cammann, K. *Fresenius J. Anal. Chem.* **1993**, 346, 420.
 19. Erber, D.; Quick, L.; Winter, F.; Roth, J.; Cammann, K. *Fresenius J. Anal. Chem.* **1994**, 349(7), 502.
 20. Erber, D.; Cammann, K. *J. AOAC International* **1997**, 80, 1084.
 21. Erber, D.; Roth, J.; Cammann, K. *Fresenius J. Anal. Chem.* **1997**, 358(5), 385.
 22. Capka, V.; Bowers, C. P.; Narvesen, J. N.; Rossi, R. F. *Talanta* **2004**, 64, 869.
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