SIMULTANEOUS DETERMINATION OF SMALL AMOUNTS OF HYDRO-CHLORIC AND HYDROBROMIC ACIDS BY DERIVATIZATION WITH ETHYLENE OXIDE AND GAS CHROMATOGRAPHY

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(First received February 10th 1983; revised manuscript received March 18th, 1983)

SUMMARY

A method has been developed to determine quantitatively micromole amounts of hydrochloric and hydrobromic acids by derivatizing the acids with ethylene oxide and determining the 2-haloethanols by gas chromatography. The advantages of the method are that chloride and bromide are determined simultaneously and that only small amounts of samples and reagents are required. Hydrobromic acid can be analyzed over the concentration range from $1 \cdot 10^{-1}$ to $5 \cdot 10^{-4}$ M and hydrochloric acid from $1 \cdot 10^{-1}$ to $2 \cdot 10^{-4}$ M. Derivatizations can be performed on 0.5 ml of solution. At $5 \cdot 10^{-4}$ M, this volume contains 0.25 μmole of halide. The relative precision of the method is 3–10 % at the 95 % confidence limit.

The method is applicable to a number of analytical problems and provides a means of measuring the amounts of hydrochloric and hydrobromic acids evolved during the combustion of flame-retarded polymers in a Schöniger flask. Samples weighing 10–200 mg and containing *ca.* 1–20 % (w/w) total halogens have been analyzed.

INTRODUCTION

Small amounts of HCl, HBr, and HI can be determined by treating the acids with a 1,2-olefin epoxide and quantifying the corresponding haloalcohols by gas chromatography (GC) as first reported by Russel[1]. Despite the indication that the method would be useful for simultaneous determination of the halides, subsequent published work has pertained only to the analysis of HCl: Petruj *et al.*[2] determined small amounts of HCl in chlorinated organic solvents by direct reaction of the solvents with gaseous ethylene oxide and GC determination of the 2-chloroethanol. Vierkorn-Rudolph and co-workers[3–5] have undertaken detailed studies of the reaction of HCl with a number of epoxides, with the goal of obtaining sufficient sensitivity to measure HCl in samples of air from the upper troposphere. This paper reports the development of a method for the simultaneous, quantitative analysis of HCl and HBr as their haloethanols.

In addition to the fact that the halides are simultaneously determined, the

primary advantages of the method are its sensitivity and the requirement of only small amounts of samples and reagents. About 0.5 ml of solution is required for derivatization, and quantitative results can be obtained to a lower limit of *ca.* $5 \cdot 10^{-4}$ *M*. Semiquantitative results can be obtained to *ca.* 10^{-5} *M*.

The method is generally applicable to analyses of solutions in which halide ions are present as their hydrohalic acids and was developed specifically in order to satisfy the requirements for measuring the amounts of HCl and HBr released in small-scale laboratory tests of flame-retarded materials containing both chlorinated and brominated compounds*. For these tests, such as combustion in a Schöniger flask, gases evolved during combustion or pyrolysis of milligram amounts of material are collected in a small volume of an aqueous absorbent which is subsequently analyzed. It is therefore necessary to determine bromide and chloride simultaneously at concentrations of *ca.* 10^{-2}–10^{-4} *M* in sample volumes of *ca.* 10 ml. Also, since materials being studied include formulations based on poly(vinyl chloride), chlorinated polyethylene, and polyethylene, which can release large and widely varying amounts of HCl and/or CO_2 when burned, it is necessary that the determination of Br^- be unaffected by large excesses of Cl^-, and that all methods be insensitive to excess CO_2 and to variations in pH.

Because of these requirements, a number of other analytical methods were not applicable. For example, neither classical gravimetric and titrimetric methods nor ion-selective electrodes[6]** have sufficient sensitivity and selectivity under the conditions described above. Direct GC determination of small amounts of HCl and HBr is not feasible for several reasons: the poor sensitivity of thermal conductivity detectors; the need for special detector filaments and for materials not corroded by HCl and HBr; and the tendency of HCl and HBr to produce tailing, asymmetric peaks from which it is difficult to obtain quantitative data. Other indirect GC methods employing derivatization of halide ions and flame-ionization and electron-capture detectors are not suitable because they use potentially hazardous organo-mercury compounds[7], need relatively large and concentrated samples[8], require non-aqueous solvents[9], or are appropriate for bromide and iodide, but not for chloride[10].

Although the requirements listed previously can also be satisfied by ion chromatography[11,12], this relatively new and still-evolving variant of ion-exchange chromatography employs columns of specially modified and sometimes proprietary resins and requires the use of extensively modified high-performance liquid chromatographs or dedicated ion chromatographs. For applications not requiring the greater sensitivity obtainable with ion chromatography and for laboratories not performing large numbers of routine analyses for ions, the indirect GC method can offer advantages in terms of simplicity, economy, and availability of materials and instrumentation.

The remainder of this paper will present procedures for analyses in aqueous solutions. Results from analyses of two flame-retarded materials will be presented to illustrate applications of the method.

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* It is assumed that the sole source of halide in the absorbent is the HCl and HBr evolved by combustion, since no inorganic halides are present in the formulations being studied.

** Although ion-selective electrodes have been used to determine Br^- and Cl^- in coal samples combusted in an oxygen bomb, *ca.* 1 g of material was needed and it could be inferred from the author's discussion that the method lacked the sensitivity for use with milligram samples, such as combusted in a Schöniger flask.

EXPERIMENTAL

Derivatization

n-Pentanol, as an internal standard, and HNO_3, as a catalyst, are added to solutions just prior to derivatization. A 1.0-ml aliquot of a solution which is 0.006 *M* in *n*-pentanol and 0.94 *M* in nitric acid is added to 5.0 ml of the sample. A 0.5-ml aliquot of this solution is placed in a 1-ml micro-reaction vial (Pierce) with a magnetic stirrer and is sealed with a PTFE-lined silicone septum and screw cap.

Ethylene oxide from a lecture bottle is introduced into the vial through a 22-gauge stainless-steel needle and is bubbled into the solution for 5 min. Another 22-gauge needle is inserted into the headspace of the vial for 5 sec per minute to release the pressure. Sealed vials are heated in a constant temperature bath at 45°C and the solutions stirred for 1 h. Venting needles are then inserted into the headspace, and the solutions are stirred at room temperature overnight.

Gas chromatography

Samples are analyzed on a 6 ft. × 1/8 in. I.D. stainless steel column packed with 10% Carbowax K20M on 80–100 mesh Chromosorb W AW DMCS. The gas chromatograph (Perkin-Elmer 990) is equipped with dual columns, dual flame ionization detectors, and an electrometer operated in the differential mode for column compensation. Helium is the carrier gas at 30 ml/min. Samples (0.1 *μ*l) are injected into a glass-lined injector port at 200°C. The column oven is held at 120°C for 8 min, heated to 175°C at 24°C/min and held at 175°C for 25 min. The manifold is at 250°C. Graphical and numerical data are obtained on a Hewlett-Packard 3390A recording integrator.

Quantitation

A series of eight standard solutions of reagent grade HCl and HBr are prepared at concentrations from 0.0005 *M* to 0.1 *M*. The standard solutions are derivatized and then chromatographed according to the procedures outlined above. For each acid at each concentration, a ratio is calculated from the areas of the haloethanol and *n*-pentanol peaks. These ratios are plotted *versus* concentration of acid to construct calibration curves.

Sample preparation for combustion studies

Weighed samples (from 10 to 200 mg, depending on the composition of the samples) are enclosed in ashless paper wrappers (Whatman No. 42). A 1000-ml Schöniger flask (A. H. Thomas) is flushed with oxygen for 3 min, charged with 10.0 ml of distilled water and flushed with oxygen for an additional minute. The samples are burned in accordance with the manufacturer's instructions and the flasks are stored unopened at room temperature overnight. The absorbents are filtered through a 0.45 *μ*m filter (Millex-HA, Millipore) and stored in glass vials with polyethylene-lined screw caps. Aliquots of the solutions are derivatized and chromatographed as outlined above.

RESULTS

Chromatograms for standard solutions of derivatized HCl and HBr are shown in Fig. 1a and b. The peaks for excess ethylene oxide, n-pentanol, 2-chloro- and 2-bromoethanol are eluted isothermally at 120°C. The larger peaks eluting at longer retention times are ethylene glycol and higher-molecular-weight glycols formed from excess ethylene oxide in acidic aqueous solution.

The identification of the chloro- and bromoethanol peaks at 3.1 and 5.9 min was confirmed by GC–mass spectrometry (MS) analyses[13] of the derivatized solutions of HCl and HBr and of reagent-grade 2-chloroethanol and 2-bromoethanol (Aldrich). No other compounds were detected co-eluting with the haloethanols in any of the solutions. However, chromatograms of the standard haloethanols showed several additional peaks, comprising ca. 2% of the total area, which interfered with the quantitation of the n-pentanol standard. Therefore, calibration curves were constructed from derivatized solutions of HCl and HBr rather than from primary standards.

Fig. 1c is the chromatogram of a blank from a derivatized solution of 0.001 M pentanol and 0.16 M nitric acid. There is a small peak with the same retention time as
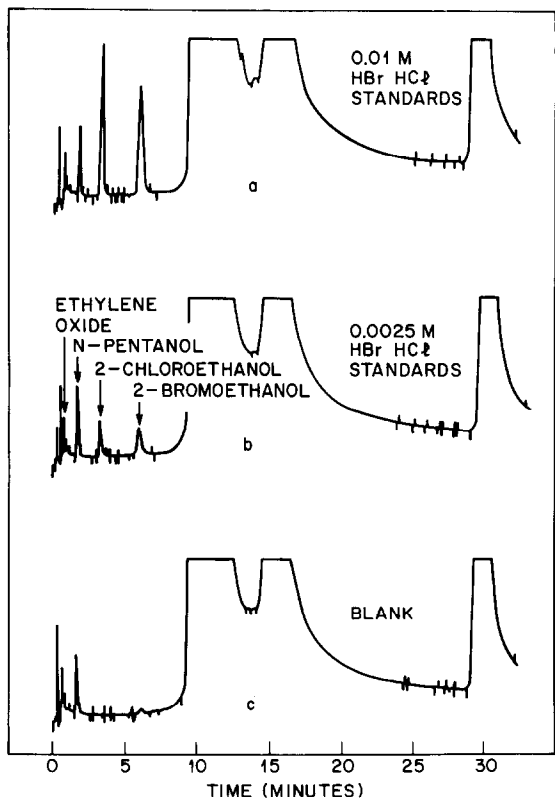

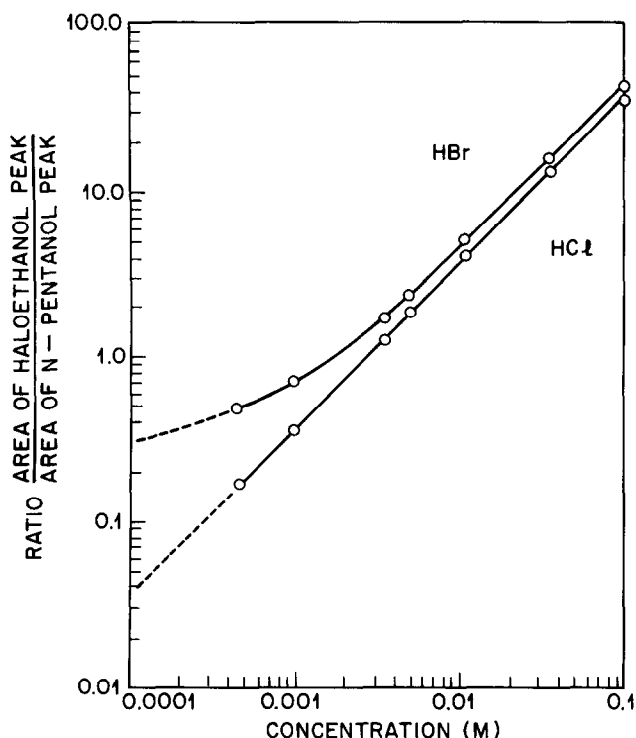Fig. 1. Chromatograms of derivatized HBr and HCl standards and a blank.

Fig. 2. Calibration curves for derivatized HBr and HCl standards.

bromoethanol and and an average area corresponding to about $1.2 \cdot 10^{-4}$ M HBr. Efforts to identify this peak by GC–MS have been unsuccessful.

Calibration curves of HCl and HBr are shown in Fig. 2. The curve for HBr is not linear at low concentrations due to the contribution of the small peak in the blank. However, the working calibration curve extends to at least $5 \cdot 10^{-4}$ M. The calibration curve for HCl is linear to at least $2 \cdot 10^{-4}$ M.

The most significant source of error in the determination appears to be the derivatization reaction. For eight determinations of one derivatized standard solution, the average R.S.D. for both HCl and HBr was 3 %. However, for determinations of seven different derivatizations of this one standard solution, the R.S.D. was 10 %. On the average, the R.S.D. is 10–12 % at 0.001 M and 3–8 % at 0.01 M.

Fig. 3a and b are chromatograms of two flame-retarded materials and are presented to illustrate an application of the method. The chromatograms are comparable to those of the standards. There are no additional peaks to interfere in the analysis. Quantitative data are summarized in Table I. Results have been converted from determined concentrations of haloacids to equivalent weight-percent halides in the original samples.

Sample A, a thermosetting molding compound, consisting of *ca.* 20 % epoxy novolac resin and 80 % silica filler, had been previously cured, crushed, and passed through a 60-mesh screen. Neutron activation analyses (NAA) had shown 0.925 ± 0.012 % Br and 256 ± 27 ppm Cl. Three samples of the powdered material were
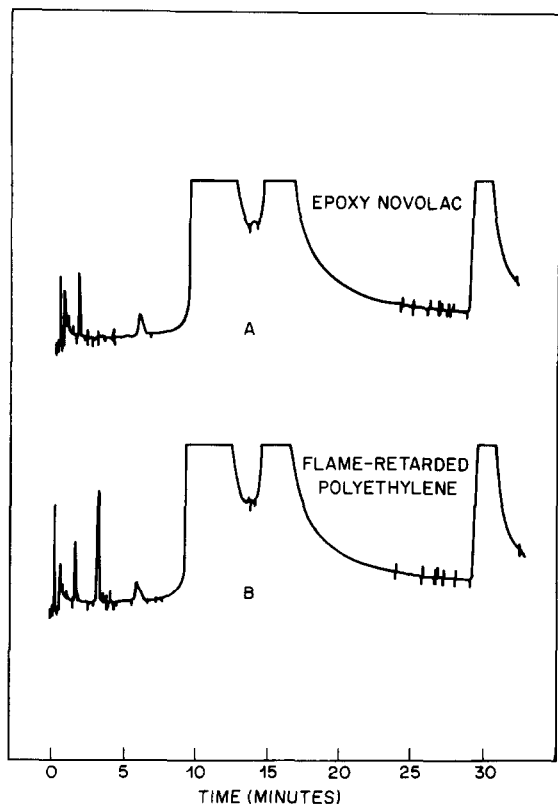
Fig. 3. Chromatograms of derivatized absorbents from burned polymers.

burned in Schöniger flasks and analyzed. The determined concentration of HBr in the absorbent corresponds to the release of $1.00 \pm 0.17\%$ (w/w) Br from the samples. At the 95% confidence level, this value is not significantly different than the 0.925% Br determined in the unburned material by NAA. Small peaks observed for chloroethanol provided semiquantitative results; $0.06 \pm 0.03\%$ Cl was determined. This is the same order of magnitude as the 0.026% found by NAA.

Sample B, a flame-retarded polyethylene had been compounded to contain 8.9% Br from decabromodiphenoxyethane and 13.6% Cl from chlorinated polyethylene. Samples B and B′ had the same nominal composition but had been processed under different conditions. B′ was darker and less flammable than B. Results for analysis of five samples of B and two samples of B′ are shown in Table I, rows I and III. Because only two samples of B′ were analyzed, results for the two of the five samples of B which were burned at the same time are shown separately in row II.

There were no significant differences in the amounts of HCl released from B and B′. Differences in the yields of HBr were significant at 90% confidence limits when two samples of each material (rows II and III) were compared and were significant at 95% when the larger sampling of B (row I) was considered. Thus, the described analytical method has made it possible to show that differences in the

TABLE I

EVOLDED Br⁻ AND Cl⁻ FROM COMBUSTION STUDIES

Sample	Br (%, w/w)			Cl (%, w/w)			R.S.D. (%)		n*
	Nominal	Determined		Nominal	Determined		Br	Cl	
		Av.	S.D.		Av.	S.D.			
A. Molding compound	0.93 ± 0.01	1.00	0.17	0.026 ± 0.003	0.06	0.03	16.5	50	3
B. FR-Polyethylene	8.9			13.6					
I. Light = B		7.60	0.94		13.74	0.44	12.3	3.2	5
II. Light = B		8.35	0.35		13.75	0.50	4.2	3.6	2**
III. Dark = B'		9.45	0.21		14.85	1.02	2.2	8.1	2

* n = number of determinations, each of which is the average of data from two chromatograms from the same solution.
** These are two of the five determinations listed above.

processing conditions, as indicated by the darkening of the polymer, have influenced the amount of Br incorporated into and/or released from this material.

DISCUSSION

Although the results presented in this report have emphasized analyses of aqueous absorbents of combustion products, the described method is also suitable for other applications. Samples of tetrabutylammonium chloride from various suppliers have been tested for contamination with bromide, and HBr has been detected in carbon tetrachloride[14]. This latter analysis extends the work of Petruj[2], who determined HCl in organic solvents. For non-aqueous solutions, the preparation of standard solutions is more difficult, but chromatograms are shorter because high-molecular-weight glycols are not formed as side products of the derivatization.

Four aspects of the experimental procedure require brief comments:

(1) We have found that addition of 0.16 M nitric acid and heating and stirring of the reaction mixture are critical for obtaining adequate sensitivity and reproducibility. Before these steps were included, quantitative results varied with the total elapsed time between derivatization and analysis and with the pH of the solution. Both modifications to the procedure increase the rate of ring-opening of the epoxide, thereby (a) ensuring the completeness of the reaction between the haloacids and epoxide and (b) promoting the consumption of excess ethylene oxide by its reaction with water to form glycol. Bächmann et al.[5] observed similar results in studies of the reaction of HCl with epibromohydrin. Also, removal of unreacted ethylene oxide is important because it bubbles into the sampling syringe and prevents accurate measurement and transfer of the sample.

(2) The stability of derivatized solutions was evaluated for a month. The haloethanol–pentanol ratios increased gradually and the areas of the glycol peaks at long retention times became significantly larger. In view of this evidence of slow, secondary reactions among residual ethylene oxide, pentanol, haloethanols, and glycols, all quantitative data are obtained within two days of derivatization.

TABLE II

MOLAR CONCENTRATIONS IN STANDARD SOLUTIONS

Solution No.	Nominal			Treatment	Determined	
	HCl	HBr	Br_2		HCl	HBr
1	0.005	0.005	—	None	0.0043	0.0047
				Extraction	0.0043	0.0045
2	0.005	0.005	0.005	None	0.0048	0.0072
				Extraction	0.0048	0.0048
3	0.005	0.005	0.001	None	0.0048	0.0055
				Extraction	0.0047	0.0049
4	0.005	0.005	0.02	None	0.0048	0.0072
				Extraction	0.0048	0.0048

(3) Among a large number of compounds evaluated for internal standards, only n-pentanol was both soluble in water and separable from the haloethanols under reasonable chromatographic conditions. it was assumed that halogenation of a primary alcohol in dilute acidic solution at room temperature would be minimal[15]. Therefore, in our initial work with standard solutions and with flame retardants containing low levels of chlorine and bromine, n-pentanol and nitric acid were added to the absorbent before combustion. However, when neat samples of a flame retardant (decabromodiphenoxyethane) containing 77 % bromine were burned, the area of the n-pentanol peak was significantly smaller than usual, suggesting a possible reaction between n-pentanol and HBr. By using distilled water as the absorbent and adding the n-pentanol and nitric acid just prior to derivatization, the area of the n-pentanol peak has been restored to reproducible values which show no evidence of significant reactions between sample and standard.

(4) There is evidence[16], that Br_2 as well as HBr can be released during the combustion of brominated organic materials in a Schöniger flask. Therefore, a series of standard solutions, summarized in Table II, were studied to determine the effect, if any, of Br_2 on the quantitation of chloride and bromide. A small and non-quantitative enhancement in the yield of bromoethanol was observed when Br_2 was added to standard solutions. However, following a two-fold extraction of Br_2 with a 2:1 excess of carbon tetrachloride, quantitative results were obtained for HBr. Alternatively, Br_2 can be reduced with hydrazine before derivatization in order to determine total bromine as bromide[16].

CONCLUSIONS

A method has been developed to determine simultaneously and quantitatively micromole amounts of HCl and HBr by treating the haloacids with ethylene oxide and determining the corresponding 2-haloethanols by GC. Advantages of the method are that chloride and bromide are determined simultaneously and that only small quantities of samples and reagents are required. HBr can be determined at concentrations as low as $5 \cdot 10^{-4}$ M and HCl at $2 \cdot 10^{-4}$ M. Derivatizations require 0.5 ml of solution. At $5 \cdot 10^{-4}$ M, this corresponds to 0.25 μmole of halide. The relative preci-

sion of the method is 3–10 %, depending on concentration. The method is applicable to a number of analytical problems and, in particular, provides a means of measuring a small amount of HCl and HBr released in small-scale tests of flame-retarded polymers containing chlorinated and brominated compounds. Samples weighing 10–200 mg and containing 1–20 % Cl and/or Br have been analyzed.

ACKNOWLEDGEMENT

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