

Note

Microdetermination of iodine in organic compounds by reversed-phase high-performance liquid chromatography

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The microdetermination of iodine in organic compounds has generally been carried out by mercurimetric titration using diphenylcarbazone as an indicator after oxygen flask combustion^{1,2}. However, interferences from other halogens in these volumetric analyses cannot be avoided especially in the detection of lower levels of iodine.

Among the wide range of methods available for the determination of inorganic anions, ion chromatographic methods^{3–7} based on both an ion-exchange separation and conductometric detection have been extensively studied in recent years. We have also tried to separate and analyze iodide ion according to such procedures. However, the iodide peak tailed badly with a very long elution time, which is probably attributed to the strong binding of analyte to the anion-exchange resin. Reversed-phase high-performance liquid chromatography (RP-HPLC) has also been applied to the determination of inorganic anions^{8–11}. Some of these interesting studies revealed that the inorganic anions were retained on the chemically bonded ODS (C₁₈) column when using tetrabutylammonium counter ions as additive to the mobile phase^{8,9}.

In the present study, we have established a reversed-phase ion-pair system for the microdetermination of iodine in organic compounds, based on UV detection after flask combustion.

EXPERIMENTAL

Chemicals

Tetrabutylammonium hydroxide (TBA-OH, 10% aqueous solution), acetonitrile and other reagents were purchased from Wako Pure Chemical Co. (Osaka, Japan). Filter-paper, No. 7, was from Toyo Roshi Co. (Tokyo, Japan). The standard iodide ion solution (100 µg/ml) was prepared by dissolving analytical grade potassium iodide (Iwai Chemical Co., Tokyo, Japan) which had been dried overnight *in vacuo* at 100°C. The test samples used for the iodine determination were *o*-iodobenzoic acid and trihaloallyl derivatives: C₆H₇O₃BrI₂, C₃H₃OBrI₂ and C₃H₃OI₃.

Procedures

Organic samples ranging from 1 to 5 mg were decomposed in a 500-ml oxygen

flask. The combusted products were dissolved in 20 ml of 2 mM sodium hydroxide containing 0.05% (w/v) hydrazine. After standing for 20 min, a 25- μ l aliquot of the solution was injected into the HPLC system.

The HPLC system consisted of a Model 655 solvent-delivery pump, a Model 638-41 variable wavelength UV detector (Hitachi, Tokyo, Japan) operating at 227 nm and a Model 710B WISP[®] automated injector (Waters Assoc., Milford, MA, U.S.A.). A reversed-phase μ Bondapak C₁₈ column (30 cm \times 3.9 mm I.D., Waters Assoc.) was used for the separation. The mobile phase was acetonitrile–2 mM TBA-OH–40 mM phosphate buffer (pH 6.0) (5.0:47.5:47.5) at a flow-rate of 1.0 ml/min. After the separation, the chromatographic data were processed by a Model 3388A reporting integrator (Hewlett-Packard, Avondale, PA, U.S.A.). The iodine content in the organic compounds was calculated from the peak area with reference to calibration standards.

RESULTS AND DISCUSSION

Separation conditions

The optimum separation conditions were obtained by varying the pH of the phosphate buffer, the concentration of TBA-OH and the acetonitrile content. The k' values were measured, where k' (capacity factor) = $(t_R - t_0)/t_0$; t_R is the retention time of I^- and t_0 is that of the unretained peak (2.50 min in this system). The TBA-OH concentration was varied from 0 to 2.0 mM while the acetonitrile content was adjusted between 1 and 10% in the 20 mM phosphate buffer of pH 6.0. The optimum concentrations for TBA-OH and acetonitrile were found to be 1 mM and 5%, respectively. The optimum pH of the phosphate buffer was found by changing the pH from 4 to 7. Fig. 1 shows the relationship between the pH and k' values. A constant and desirable k' value was observed between pH 5 and 6.

Considering the pH of the analysis solution, we chose a buffer of pH 6 as optimum for the separation. Iodide ion was successfully separated from other anions which might interfere in the analysis. The k' values were: NO_2^- , 1.06; Br^- , 1.08; NO_3^- , 1.29; CrO_4^{2-} , 1.54; I^- , 2.26 and SCN^- , 4.93. Other anions, F^- , Cl^- , PO_4^{3-} and SO_4^{2-} were not detected at 227 nm. The HPLC profiles for standard mixtures are shown in Fig. 2.

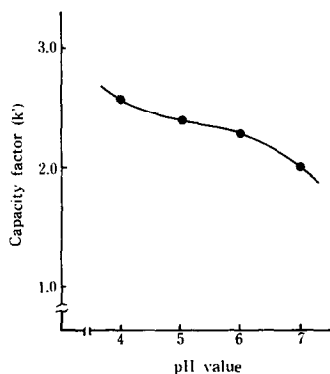


Fig. 1. Effect of eluent pH on retention. Buffer: 1 mM TBA-OH–5% acetonitrile in 20 mM phosphate buffer. Amount injected: 1 μ g I^- .

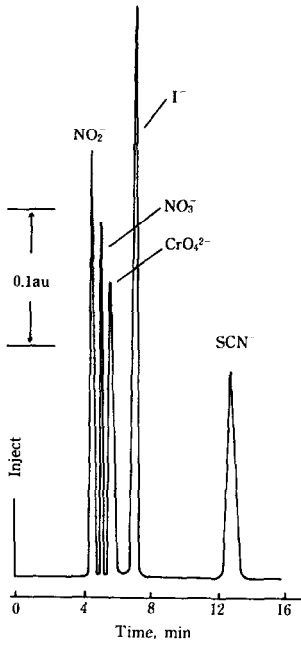


Fig. 2. HPLC chromatogram of a standard mixture. Detection: UV, 227 nm. Amount injected (μg): NO_2^- , 1; NO_3^- , 2; CrO_4^{2-} , 5; I^- , 1 and SCN^- , 2.

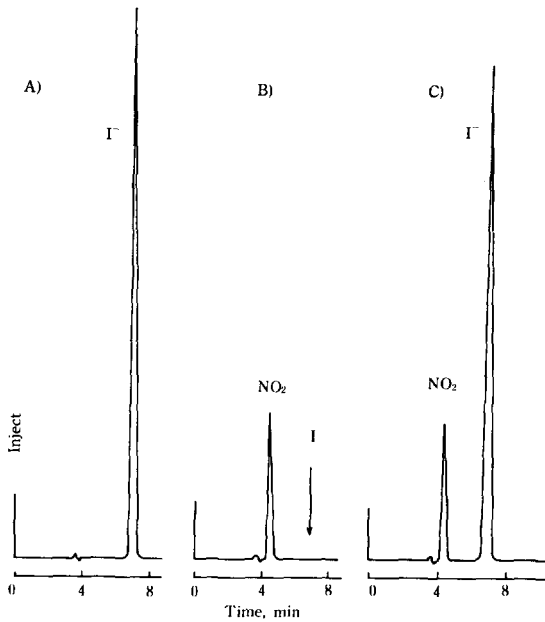


Fig. 3. HPLC chromatograms of *o*-iodobenzoic acid (3.3 mg) after oxygen flask combustion. A, Standard ($1 \mu\text{g I}^-$); B, blank (filter-paper); C, oxygen flask combusted sample.

Reproducibility and linearity

The reproducibility was checked by repetitive 25- μ l injections of 8 μ g/ml and 40 μ g/ml standard iodide solutions. The coefficients of variation (C.V.) for each level ($n = 11$) were found to be 0.18 and 0.25%, respectively. Good linearity, correlation coefficient (r) = 0.9999, was observed in the range from 4 ng to 2.0 μ g per injection ($n = 16$). The limit of detection in this system was found to be about 0.5 ng of iodide injected (signal-to-noise ratio = 3).

Determination of iodine in organic compounds

The HPLC profiles for the standard iodide ion, blank and sample (*o*-iodobenzoic acid) after the flask combustion are shown in Fig. 3. The analytical results for the test compounds containing from 51 to 88% iodine are shown in Table I. The results were in good agreement with the theoretical values for each compound, within $\pm 0.3\%$.

TABLE I
DETERMINATION OF IODINE IN ORGANIC COMPOUNDS

Compound	Sample (mg)	Found (%)	Deviation (%)	\bar{x} (%)
<i>o</i> -Iodobenzoic acid (C ₇ H ₅ O ₂ I), 51.17% I	1.726	51.26	+0.09	51.27
	1.886	51.31	+0.14	
	2.158	51.45	+0.28	
	3.295	51.25	+0.08	
	4.276	51.08	-0.09	
C ₆ H ₇ O ₃ BrI ₂ , 55.08% I	1.520	55.08	0	55.17
	2.368	55.36	+0.28	
	2.648	55.02	-0.06	
	2.969	55.23	+0.15	
	3.680	55.15	+0.07	
C ₃ H ₃ OBrI ₂ , 65.29% I	1.621	65.09	-0.20	65.28
	1.258	65.58	+0.29	
	1.909	65.18	-0.11	
	2.025	65.26	-0.03	
	2.560	65.29	0	
C ₃ H ₃ OI ₃ , 87.37% I	1.754	87.35	-0.02	87.31
	1.154	87.19	-0.18	
	2.136	87.27	-0.10	
	2.219	87.63	+0.26	
	3.419	87.12	-0.25	

A simple, accurate and selective HPLC method for the microdetermination of iodine in organic compounds was thus established. This method is well suited for either routine analysis of organic compounds or marine products containing iodine in various forms. This system will also be effective for the analysis of other anions, *i.e.*, nitrite, nitrate, chromate and thiocyanate.

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