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Separation and Identification of Volatile Iodine Compounds by Fractional Sublimation and Mass Spectrometric Analysis

M. E. Davis and W. E. Browning, Jr.

Abstract

A suspected non-elemental form of iodine was separated from a sample of elemental iodine by fractional sublimation under vacuum and was identified as methyl iodide by mass spectrometric analysis. An upper limit of 0.08% was set on the amount of methyl iodide in the elemental iodine source. The possible presence of hydrogen iodide and trace amounts of ethyl iodide was indicated. This method might be adapted profitably to the study of the chemical forms of fission-product iodine that might be accidentally released from nuclear facilities.

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Introduction

Hazards involved in releases of fission products into man's environment are of such concern that a great deal of effort is being expended to characterize the behavior of air-borne fission products and to assure that they remain safely contained. Iodine is the fission-product element that causes the greatest concern because of its volatility and its biological effects. The chemical and physical behavior of fission-product iodine has been found to be very complicated[1-3]. A contributing factor in trapping and retention problems is that different chemical forms of iodine exist under the conditions of its accidental release, and some of these are not effectively retained by conventional trapping devices[3-7]. Forms of iodine other than the element (I_2) usually are present in experimental radioiodine sources only in extremely low quantities and their identification is often difficult[8, 9]. This report describes an experiment in which a suspected non-elemental form of iodine was separated from a sample of elemental iodine and was identified as methyl iodide (CH_3I).

Experimental

Sources containing 50 to 200 milligrams of stable iodine with 2 to 10 millicuries of ^{131}I were used in iodine sorption studies[10]. Personnel of the Isotopes Division, ORNL, prepared this material by precipitation of palladium iodide from aqueous solution followed by thermal decomposition of the dried, solid palladium iodide under vacuum. The iodine evolved was trapped in a source tube cooled by liquid nitrogen. An untrapped mechanical pump provided the vacuum which was presumed to be in the range of 20 to 100 microns Hg. Upon completion of the palladium iodide decomposition, the stopcock on the tube containing the condensed iodine was closed, and this tube,

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under vacuum at liquid-nitrogen temperature, was removed, transported to another area, and installed in the fractional sublimation apparatus shown in Fig. 1. The system was evacuated to a pressure of 5 to 15 microns Hg using a mechanical vacuum pump. A small charcoal trap located between the pump and the fractionation system inhibited back flow of pump oil vapors and prevented residual iodine vapors from contaminating the pump. This charcoal trap was degassed by strong heating under vacuum before beginning the fractionation.

Fractions were collected by holding the original iodine source at a fixed low temperature and trapping any residual vapor in a clean evacuated tube which was cooled with liquid nitrogen. During transfer the vacuum pump was valved out of the system, a receiving tube was opened, and the source was opened for 3 minutes and then closed. After three additional minutes the receiving container was closed off, the system was pumped down, and a fresh receiving tube was cooled with liquid nitrogen. Fractions of volatile material were separated at source temperatures of -78, -66, -58, -40, -7, and +10°C by repeating these procedures. Temperatures were maintained by using a dry ice-trichloroethylene bath in which another tube, that held the iodine source and was equipped with a small heating coil, was immersed. In later work a thermoelectric cooler has been used more conveniently to obtain bath temperatures between -78 and +20°C. The percentage of the original source collected in each fraction was determined by counting the ^{131}I activity with a gamma-scintillation detector and associated equipment. Each fraction was then analyzed mass spectrometrically. The material was at room temperature when it was introduced into the mass spectrometer.

Results

The relative intensities of the mass peaks observed in the various fractions and in methyl iodide and hydrogen iodide standards are shown in Table 1. Also shown are the sublimation temperatures, the percentages of the total iodine collected in each fraction, and the likely species causing the various mass peaks, where deduction is straightforward. All intensities have been normalized to a value of 10 for mass 127; intensities not shown were too low to be measured at the pressures used. The standards were taken from methyl iodide, "Superior (b.p. 41-43°C)", purchased from Matheson, Coleman, and Bell, and from anhydrous hydrogen iodide (98% minimum purity) purchased from the Matheson Company. In fractions E, F, and Residue, solid iodine remained on the walls of the sample tube during injection into the mass spectrometer and only the vapor over the solid was analyzed. Hence, in fraction E the relative intensity of the methyl iodide component listed in Table 1 is probably too high since the vapor would be enriched in this volatile material. Fraction F and the residue fraction can be considered to be I_2 standards since no other mass components were significantly present. The hydrogen iodide standard appeared to have undergone some decomposition to I_2.

In all samples the prominent mass peaks can be accounted for by iodine, methyl iodide, or hydrogen iodide. Mass 156 is suggestive of ethyl iodide (C_2H_5I), but the intensity of this peak was very low and a clear mass pattern was not obtained. The presence of masses 77 and 78, which could be doubly charged species of ethyl iodide fragments, also suggest its presence. The presence of masses 79, 81, 85, 91, 92, 96 and 157 is not readily explainable in terms of iodine compounds. It is interesting to note that masses 77, 81,

91, and 156 are significantly more intense than adjacent masses in fraction D, especially when compared to the other fractions. The masses that appear at low intensities and that do not clearly represent iodine compounds could be due to hydrocarbon vapors from the decomposition of vacuum pump oil. The largest methyl iodide peak (CH_3I^+) became less prominent as sublimation temperatures were increased and disappeared altogether in both sample F and the unsublimed residue. The relative height of the hydrogen iodide mass peak (128), however, varied irregularly with the fractions collected.

Conclusions

In comparing the peak heights of masses associated with methyl iodide in the unknowns with those in the methyl iodide standard, it is apparent that fraction A is essentially all methyl iodide. The preliminary nature of this work precluded calibration of the mass spectrometer for quantitative response to the species of iodine introduced. Hence, quantitative determination of the amounts of iodine, hydrogen iodide, and methyl iodide in mixtures was not possible. We can, however, arrive at an upper limit of 0.077% methyl iodide in the original sample by taking the sum of the amounts of iodine in fractions A, B, C, and D and assuming all this material is methyl iodide. This methyl iodide is presumed to originate from the reaction of iodine with traces of organic materials during preparation of the source.

The data presented here do not permit assessment of the amount of hydrogen iodide present. This is due to several factors which include (1) the low relative intensity of the mass 128 peak (HI) in all fractions, (2) the irregular variation in mass 128 intensities in the fractions collected at the various sublimation temperatures (one would expect that hydrogen iodide, having a higher vapor pressure than methyl iodide at a given temperature,

would tend to accumulate in the lowest temperature fractions, but this was not observed), and (3) the decomposition, that was visually apparent, of the hydrogen iodide standard. One might conclude that hydrogen iodide may be present, albeit in very low quantities, wherever free iodine and a source of hydrogen, such as water, exists. Since mass 128 intensity pattern did not follow the volatility of hydrogen iodide nor the relative concentration of free iodine, its presence in low abundances might be an artifact contributed to by the ionization process within the mass spectrometer. Fragmentation of methyl iodide or combination of iodine ions with hydrogen from some other source might give rise to the traces of mass 128 appearing in all the samples analyzed. These data suggest the presence of ethyl iodide in the original sample to the extent of less than 1% of that observed for methyl iodide.

The techniques discussed here permitted identification of methyl iodide which was present in iodine to a maximum extent of 0.08% and indicated the possible presence of trace amounts of ethyl iodide. The sensitivity of this method indicates that it might be profitably adapted to the study of the various chemical forms of fission-product iodine that might be accidentally released from nuclear facilities of all types. It is very likely that knowledge gained in more extensive use of these techniques could lead to improvements in sensitivity and to an increase in the information that can be obtained from such mass-spectrometric data.

Acknowledgements

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Table 1. Relative Intensities of Masses Observed in Standards and in the Iodine Fractionation Experiments

Fraction		A	B	C	D	E	F	Residue	Standards CH_3I	Standards HI
Sublimation Temp. °C		-78	-66	-58	-40	-7	+10			
Percentage of Total Iodine		0.015	0.017	0.005*	0.039	3.32	91.2	5.41		
Mass	Likely Species									
63.5	I^{++}	0.40	0.64	0.79	0.98	0.33		0.38	1.1	0.63
64	HI^{++}									0.26
65		0.09	0.05	0.64	0.46					
71	CH_3I^{++}								1.3	
77	$C_2H_3I^{++}$	0.82	0.21	0.43	1.5	0.07		0.01		
78	$C_2H_5I^{++}$	0.80	0.27	0.32	0.21	0.01				
79		0.16	0.07	0.46	0.72	0.03				
81		0.11	0.07	0.71	1.3	0.08				
85						0.03				
91		0.49	0.23	0.43	1.7	0.01				
92		0.37	0.11	2.0	0.96	0.01				
96						0.01				
127	I^+, I_2^{++}	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
128	HI^+	0.98	1.3	2.9	2.1	0.83	0.10	0.99	0.62	4.1
139	CI^+	0.98	0.85	1.1	1.1	0.02			1.3	
140	CHI^+	0.80	0.64	0.86	0.8	0.01			1.0	
141	CH_2I^+	2.9	2.3	2.5	2.2	0.03			3.6	
142	CH_3I^+	26.4	18.1	19.2	13.8	0.23			26.6	
155	$C_2H_4I^+$	0.35	0.16		0.11	0.07				
156	$C_2H_5I^+$	0.04	0.03		0.32	0.01				
157		0.20	0.11		0.11	0.03				
254	I_2^+					42.1	40.3	41.6		34.2

* The small amount of iodine collected at -58°C can be attributed to the fact that some of the volatile material was inadvertently pumped off.

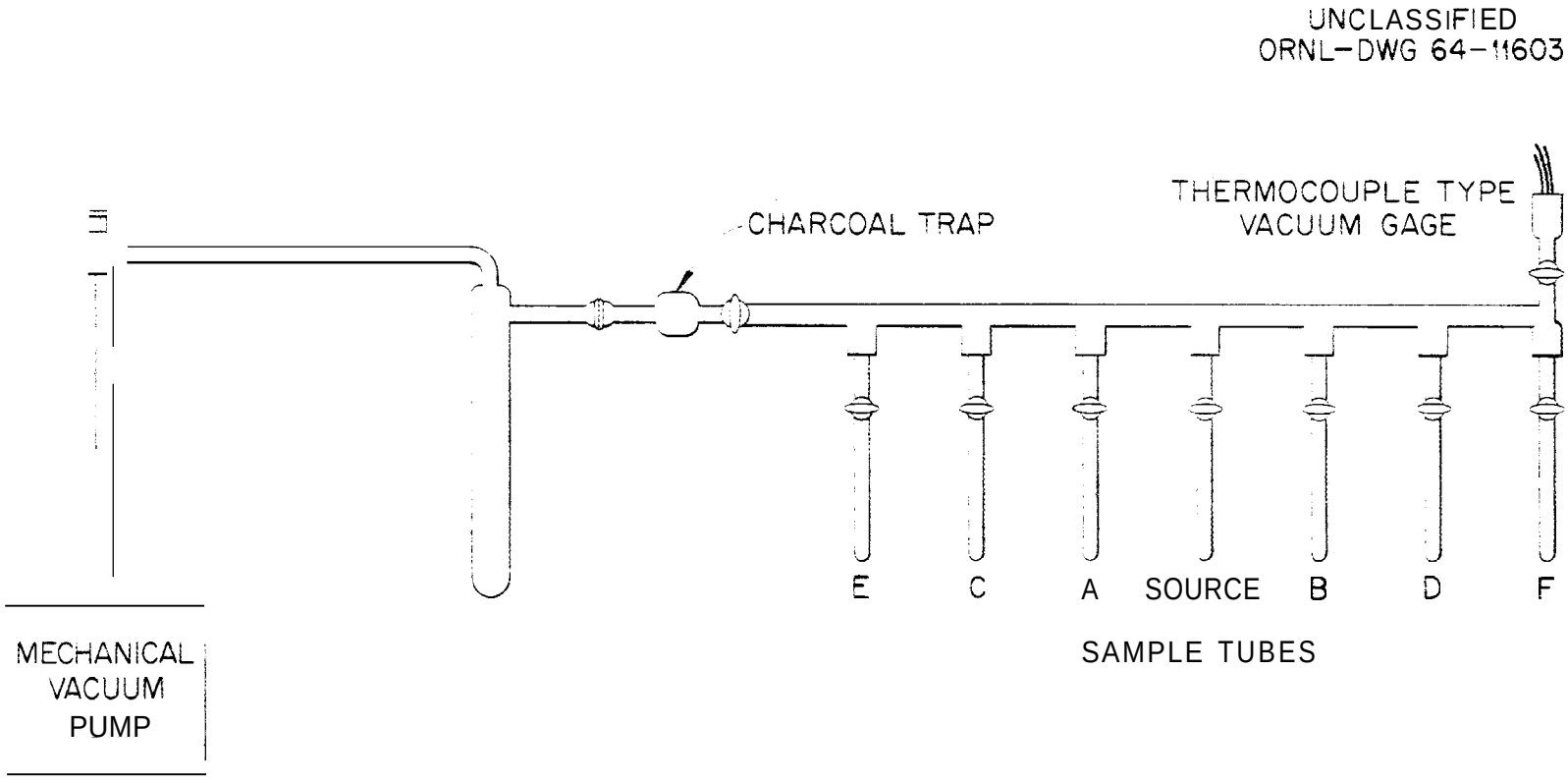

Fig. 1. Iodine Fractional Sublimation Apparatus.

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