Journal of Chromatography, 437 (1988) 322–327
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 194

Note

Analyses of impurities in methamphetamine by inductively coupled plasma mass spectrometry and ion chromatography

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(Received October 26th, 1987)

The abuse of methamphetamine is a serious drug problem in Japan. Almost all this methamphetamine seems to be imported illegally from other countries. The methamphetamine of abuse in the United States and Europe is synthesized from benzyl methyl ketone as a starting material by the Laukert reaction. On the other hand, this drug seized in Japan seems to be synthesized from ephedrine by a one- or two-step reduction in clandestine laboratories[1]. For samples from the United States and Europe, there have been many reports concerning the organic impurities in methamphetamine, and it is possible to identify the origin of the samples by analyses of the organic impurities by gas chromatography and gas chromatography–mass spectrometry[2–9]. However, the methamphetamine seized in Japan is quite pure as regards organic impurities. It is very difficult to discriminate such samples by analyses of the organic impurities[10]. For this reason, the inorganic impurities in methamphetamine have also been investigated, using nuclear activation analysis[1].

In 1975, the concept of inductively coupled plasma mass spectrometry (ICP-MS) was introduced by Gray[11], and in the 1980s an ICP-MS instrument was developed by Houks[12]. This method is characterized by its high sensitivity and accurate quantitative analyses compared with other multi-element analyses[13,14]. These characteristics were considered to be useful in forensic laboratories.

In this paper, the analyses by ICP-MS and ion chromatography (IC) of inorganic impurities in methamphetamine seized in Japan are presented, and the possibility of discrimination by these analyses is discussed.

EXPERIMENTAL

Materials

The distilled/deionized water used in this work was obtained by feeding laboratory distilled water through a Millipore Multi-Q water-purification system (Millipore, Bedford, MA, U.S.A.). All other chemicals and reagents were of analytical grade.

Inductively coupled plasma mass spectrometry

The spectrometer used for these analyses was a Model PMS 100 ICP-MS system (Yokogawa Electric Corp., Tokyo, Japan). The plasma operating conditions were: radiofrequency power, 1.5 kW; nebulizer gas flow-rate, 0.9 l/min; plasma gas flow-rate, 14 l/min; auxiliary gas flow-rate, 0.4 l/min. The plasma was sampled at a depth of 10 mm from the load coil.

ICP-MS analysis of methamphetamine impurities

The methamphetamine crystals were dissolved in distilled/deionized water and to give a 0.1% solution. This solution was introduced through the nebulizer into the ICP-MS system.

Ion chromatography

Ion chromatography was performed with a Model IC 500 ion chromatoanalyzer system equipped with a conductivity detector (Yokogawa). The column used for separation was a SAM3-125 anion-exchange column and a pre-column, PAM3-035 (Yokogawa), was also used. The eluent was 4.4 m*M* sodium carbonate + 1.2 m*M* sodium bicarbonate with flow-rate of 2 ml/min. Sample crystals were dissolved in distilled/deionized water to give a 0.1% solution and 50 μl were injected into the analyzer system.

RESULTS

Calibration graphs and detection limits

The calibration graphs were prepared for the elements Na, Pd, Ba, I and Br. These elements had previously been detected in methamphetamine crystals by neutron activation analysis[1]. The calibration graphs are shown in Figs. 1 and 2. Those of Na and Br were prepared within the range 0–100 ppb* and those of Pd, Ba and I from 0 to 4 ppb. The graphs showed good linearity with a 10^6 dynamic range under these conditions. The detection limits for Na, Pd, Ba, I and Br were 0.03, 0.04, 0.005, 0.03 and 0.08 ppb, respectively.

ICP-MS spectra of the control distilled/deionized water and of a solution of seized methamphetamine are shown in Fig. 3. In the spectra of the former sample, at $m/z < 80$, peaks caused by argon and air were observed. Some of these ions were assigned to $^{40}Ar_2^+$ (m/z 80), $^{40}ArO^+$ (m/z 56) and $^{40}ArH^+$ (m/z 41). Other peaks at $m/z < 40$ were caused by O_2^+ (m/z 32), O^+ (m/z 16) and NO^+ (m/z 30).

In the ICP-MS spectra of the methamphetamine solution, besides Na, Pd, Ba, I and Br, several other elemets were detected in minor amounts. The elements detected in each sample are shown in Table I, and the contents of the major elements, Na, Pd, Ba, I and Br, are summarized in Table II.

* Throughout this article the American billion (10^9) is meant.

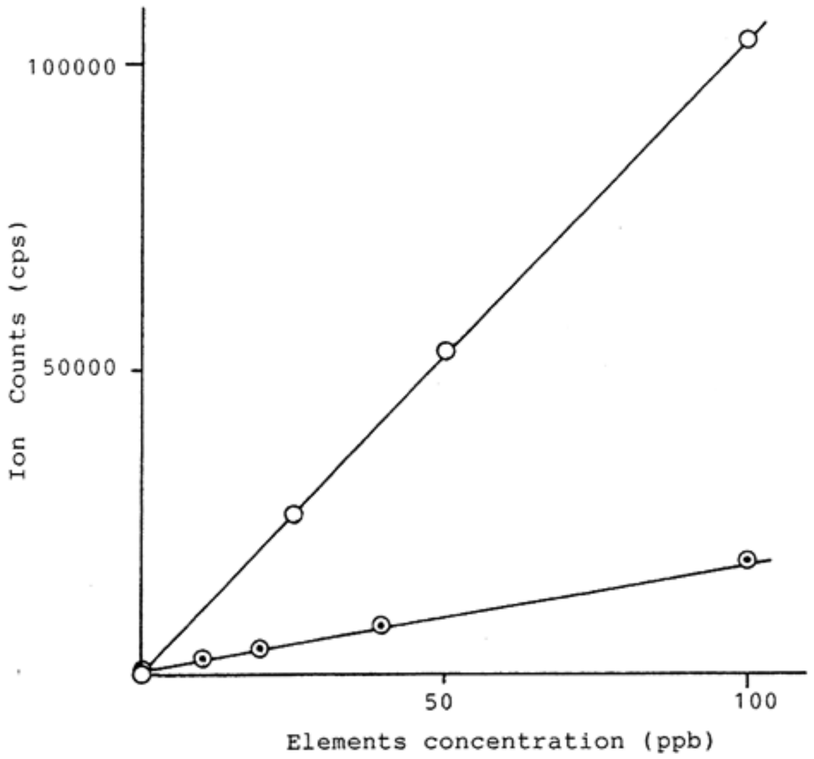

Fig. 1. Calibration graphs for Na (○—○) and Br (⊙—⊙).

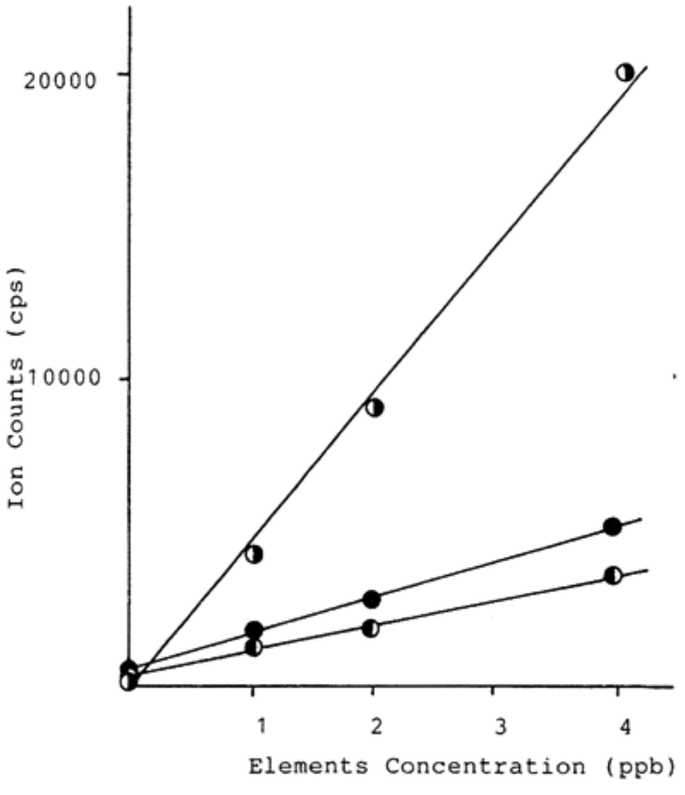

Fig. 2. Calibration graphs for Pd (◐—◐), Ba (◑—◑) and I (●—●).

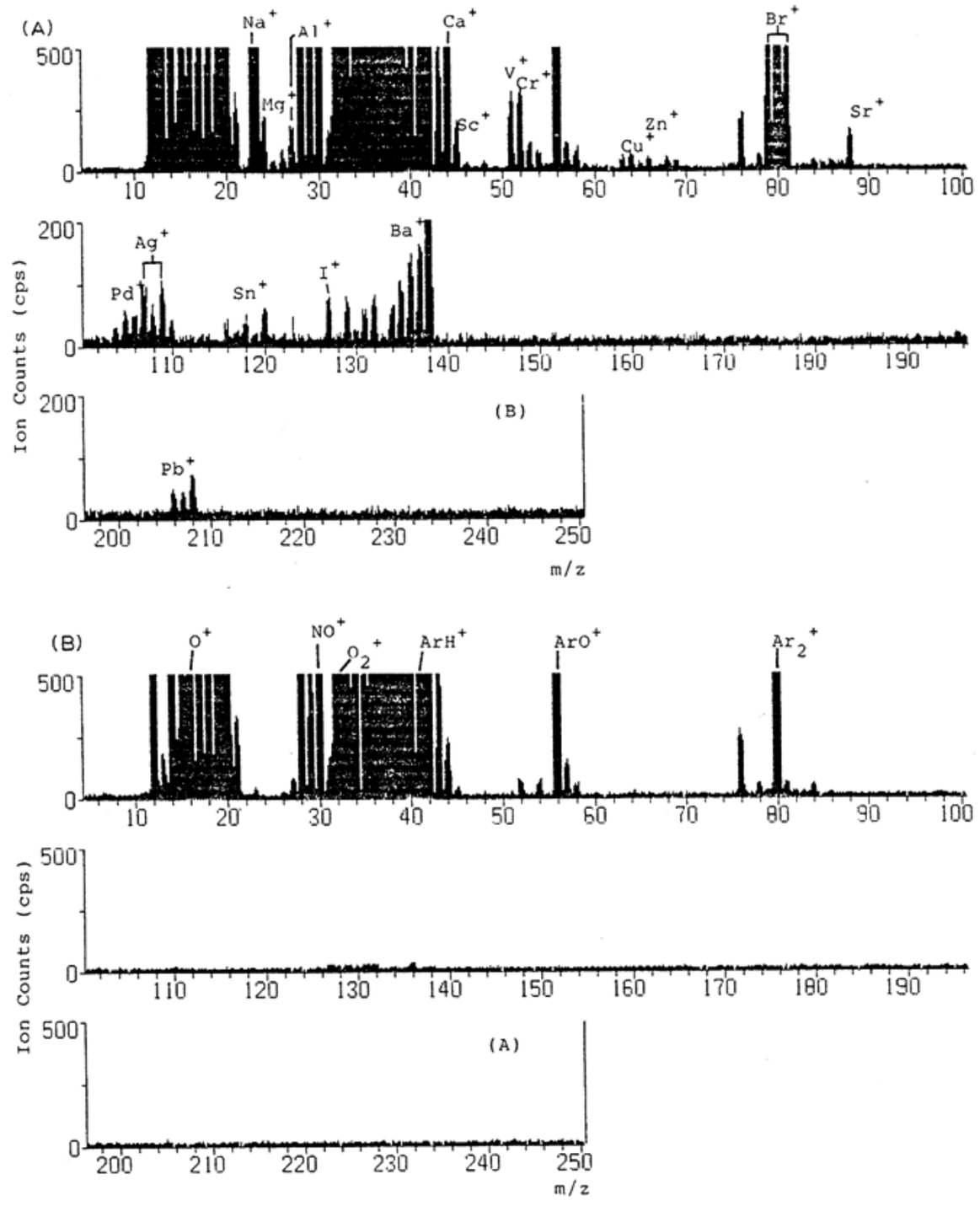

Fig. 3. Inductively coupled plasma mass spectra of distilled/deionized water (A) and of methamphetamine (B).

In Table I, samples 2(1) and 2(2) were collected from different positions of the same large crystal: 2(1) from the surface and 2(2) from the interior. The elements detected were not very different from each other, but as shown in Table II a large difference was observed in the contents of the major elements. The contents in the surface were much higher than those in the interior, especially for Na.

TABLE I

ELEMENTS DETECTED IN SEIZED METHAMPHETAMINE BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Sample No.	*Elements detected*
1	Na,Mg,Al,Si,Cl,Ca,Sc,Ti,V,Cr, Zn,Br,Sr, I,Ba,Pb
2(1)	Na,Mg,Al,Si,Cl,Ca,Sc, V,Cr,Cu,Zn,Br,Sr,Ag,Pd,Sn,I,Ba,Pd
2(2)	Na,Mg,Al,Si,Cl,Ca,Sc, V,Cr,Cu,Zn,Br,Sr, Pd, I,Ba,Pb

TABLE II

CONTENTS OF MAJOR ELEMENTS IN SEIZED METHAMPHETAMINE

n.d. = Not detected.

Sample No.	*Na(ppm)*	*Pd(ppb)*	*Ba(ppm)*	*I(ppm)*	*Br(ppm)*
1	2200	n.d.	1.0	190	15
2(1)	3500	1000	3.2	350	180
2(2)	870	460	2.4	320	68
3	2100	3000	8.1	n.d.	90
4	3500	220	6.1	n.d.	62

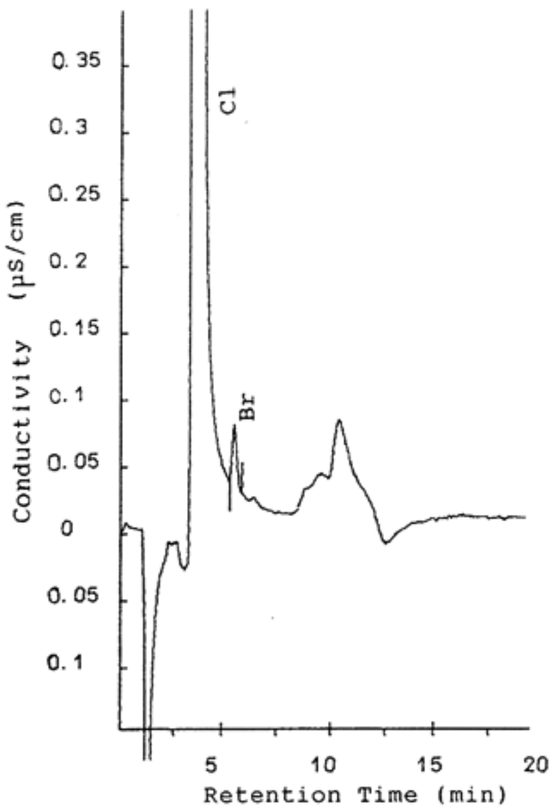

Fig. 4. Ion chromatogram of methamphetamine.

Ion chromatography of methamphetamine crystals

The anions in the crystal were also investigated by IC. Screening was performed for F, Cl, Br, I, NO_2, NO_3, SO_4 and PO_4 and the detection limits were from 4 to 60 ppb. A typical ion chromatogram of a methamphetamine sample is shown in Fig. 4, Chloride and Br were detected in all samples, and the bromide contents in samples 1, 2(1) and 2(2), were 11.2, 114.0 and 44.1 ppm, respectively.

DISCUSSION

ICP-MS is a practical method not only for qualitative analysis but also for quantitative analysis of inorganic elements. This method is characterized by its high sensitivity and conventionality compared with nuclear activation analysis and atomic absorption spectroscopy, because in Japan, nuclear activation analysis can be conducted only in the laboratories permitted by the government. Furthermore, qualitative analysis within the range from m/z 10 to 250 was performed in only 2 min. These characteristics were required in forensic science and toxicology.

In ICP-MS of methamphetamine crystals, the location of the target elements is the most serious problem; in our experiments, large variations were observed in the same crystal. Methods for decreasing this variation were required; for this purpose, the sample collection should be performed in several parts of the crystal in order to reflect the character of the whole crystal.

In IC of these samples, the chloride concentrations were especially high, but other than this, only bromide was detected. This was due to the difference in detection limits of the elements. The difference between the bromide contents obtained by the two methods could be explained by the fact that in IC the elements detected were required to be ionized under the analytical conditions, but in ICP-MS the contents determined represented the total bromide existing in the crystal. IC was considered to be a useful method for forensic chemistry. With the combination of these two methods, it may be possible to discriminate methamphetamine crystals by the contents of inorganic elements and specific elements.

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