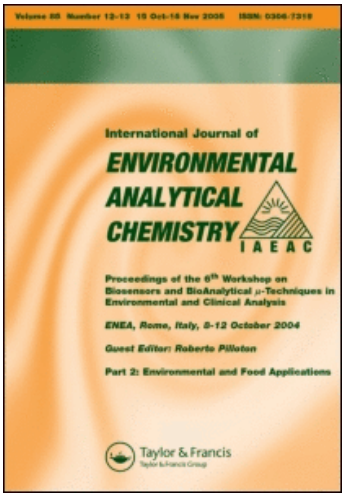

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Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to Multi-Element Analysis of Human Organs

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APPLICATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) TO MULTI-ELEMENT ANALYSIS OF HUMAN ORGANS

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Elemental concentrations of internal organs (cerebrum, cerebellum, heart, spleen, liver and kidney) of Japanese were measured with inductively coupled plasma mass spectrometry (ICP-MS). Sixty-one elements were determined simultaneously, and concentrations of some trace elements in human organs, on which information are scarcely available in the literature, were obtained. The analytical values obtained by ICP-MS and those by other methods were compared and fairly good agreement was found for Cd, Zn and Fe. Moderate agreement was found for Se and Hg, but discrepancy was observed for Mg and Na. Unacceptable values were obtained for some elements, such as Ti, Sc or Ge, probably due to polyatomic molecular interference.

KEY WORDS: ICP-MS, multi-element analysis, human organ, contamination, polyatomic molecular interference.

INTRODUCTION

An increasing number of chemicals containing trace elements are being used as materials in a variety of industries, in particular in the high-technology industries.[1] The health impacts of these trace elements must be evaluated in terms of occupational health as well as of environmental health. Wastes from these industries and the popularized high-technology products will be sources of exposure to these trace elements in general population. Therefore, it is an urgent issue to get information on the accumulation of such elements in humans, since it will give us the knowledge on the "natural level" of the elements and it will also provide a basis for toxicological research.

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Inductively coupled plasma mass spectrometry (ICP-MS) is a newly developed analytical method with capability of simultaneous multi-element analysis and with high sensitivity for most elements.[2] ICP-MS is, thus, considered to be suitable for the purpose mentioned above, i.e., to detect a variety of elements in human organs with the "natural level". However, at present, the validity of the analytical data obtained by ICP-MS has not yet been fully evaluated. In addition, some analytical problems inherent to multi-element determination by this method are becoming evident.[3–5] Polyatomic molecular interference is one of the major problems and it is partly dependent on the sample matrix. Thus, application of ICP-MS to biological materials must be examined while taking this problem into consideration. Recently we conducted multi-element analysis of human liver and kidney with ICP-MS and showed the pontial of this method as well as the indication of previously unknown polyatomic molecular interference.[6] The present paper describes the elemental composition of other organs (cerebrum, cerebellum, heart and spleen) in addition to liver and kidney employing ICP-MS. Further, data obtained by ICP-MS are compared with those by other analytical methods. Some problems in the multi-element determination of human organs with this method, including polyatomic molecular interference, are also referred.

MATERIALS AND METHODS

Cerebrum, cerebellum, heart, spleen, liver and kidney samples analyzed were obtained from 45 Japanese cadavers (age: 2 mths–82 yrs, 31 males and 14 females) autopsied at Department of Forensic Medicine, Faculty of Medicine, University of Tokyo during November 1986–August 1987. Causes of death of the present subjects were mainly arising from accidents and no known occupational exposure to metals were recognized. Trace element concentrations, measured by ICP atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS) and fluorometry, in the organs of the present subjects have been reported elsewhere.[7,8] The procedure for sample preparation is given in the literature and that for ICP-MS analysis has been described in our previous study.[6] It is briefly given here: samples were washed, weighed, digested in a PTFE-lined stainless-steel "bomb" (Uniseal Decomposition Vessel Co. Ltd.) with nitric acid (semiconductor use, Nakarai Chemicals Co. Ltd., no further purification) and diluted to 10 ml with distilled water. Five ml of the sample solution was transferred to Teflon beaker and evaporated to a volume of approximately 0.1 ml on the hot plate (140 °C) in class 100 clean bench and re-diluted to 5 ml with distilled water. Mass spectra of the samples were obtained by qualitative mode of the apparatus (ICP-MS, PMS-100, Yokogawa Electric Co. Ltd.). The concentrations of 61 elements were measured by ICP-MS using quantitative mode. Operational parameters of the apparatus has also been given in the previous paper.[6] Elements analyzed are shown in Table 1. Standard Reference Material (SRM, Bovine Liver: NBS 1577a) was analyzed concomitantly to check the accuracy of determination. Analytical results were generally in agreement with certified values except for some elements, e.g., Mg and As.[6]

Table 1 Elements analyzed, number of samples and number of samples with the concentration above lower limit of determination of the present study

Element (m/z)	*Cerebrum white matter*	*Cerebrum grey matter*	*Cerebellum*	*Heart*	*Spleen*	*Liver*	*Kidney cortex*	*Kidney medulla*	*LLD*[a]
Li(7)	0/23(0)[b]	0/23(0)	0/26(0)	0/39(0)	0/43(0)	0/44(0)	0/40(0)	1/37(3)	9.4
Be(9)	16/23(70)	8/23(35)	15/26(58)	22/39(56)	21/43(49)	21/44(48)	0/40(0)	2/37(5)	2.8
Na(23)	NA[c]	NA	26/26(100)	38/39(97)	43/43(100)	NA	40/40(100)	37/37(100)	76×10^3
Mg(24)	NA	NA	26/26(100)	39/39(100)	43/43(100)	NA	40/40(100)	37/37(100)	1.6×10^3
Al(27)	2/23(9)	0/23(0)	0/26(0)	5/39(13)	0/43(0)	3/44(7)	5/40(13)	0/37(0)	1.1×10^3
Sc(45)	23/23(100)	23/23(100)	26/26(100)	39/39(100)	43/43(100)	44/44(100)	40/40(100)	37/37(100)	15
Ti(47)	23/23(100)	23/23(100)	26/26(100)	39/39(100)	43/43(100)	44/44(100)	40/40(100)	37/37(100)	830
V(51)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	0/43(0)	1/44(2)	1/40(3)	0/37(0)	32
Cr(53)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	0/43(0)	0/44(0)	1/40(3)	0/37(0)	6.4×10^3
Mn(55)	1/23(4)	0/23(0)	1/26(4)	6/39(15)	34/43(79)	36/44(82)	34/40(85)	8/37(22)	550
Fe(57)	NA	NA	13/26(50)	28/39(72)	43/43(100)	NA	28/40(70)	19/37(51)	31×10^3
Co(59)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	0/43(0)	2/44(5)	1/40(3)	0/37(0)	84
Ni(60)	0/23(0)	0/23(0)	0/26(0)	1/39(3)	0/43(0)	0/44(0)	1/40(3)	0/37(0)	3.4×10^3
Cu(63)	NA	NA	16/26(62)	13/39(33)	1/43(2)	NA	7/40(18)	1/37(3)	3.6×10^3
Zn(66)	NA	NA	26/26(100)	39/39(100)	43/43(100)	NA	40/40(100)	37/37(100)	2.5×10^3
Ga(69)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	0/43(0)	0/44(0)	0/40(0)	0/37(0)	110
Ge(72)	4/23(17)	6/23(26)	13/26(50)	37/39(95)	43/43(100)	42/44(95)	31/40(78)	19/37(51)	17
As(75)	6/23(26)	2/23(9)	2/26(8)	16/39(41)	14/43(33)	23/44(52)	36/40(90)	20/37(54)	14
Se(82)	11/23(48)	17/23(74)	17/26(65)	37/39(95)	41/43(95)	44/44(100)	40/40(100)	37/37(100)	68
Rb(85)	23/23(100)	23/23(100)	26/26(100)	39/39(100)	43/43(100)	44/44(100)	40/40(100)	37/37(100)	40
Sr(88)	7/23(30)	9/23(39)	17/26(65)	37/39(95)	39/43(91)	19/44(43)	40/40(100)	29/37(78)	15
Y(89)	0/23(0)	0/23(0)	0/26(0)	1/39(3)	3/43(7)	4/44(9)	3/40(8)	3/37(8)	2.0
Zr(90)	4/23(17)	0/23(0)	1/26(4)	8/39(21)	8/43(19)	6/44(14)	5/40(13)	2/37(5)	65
Nb(93)	0/23(0)	0/23(0)	0/26(0)	1/39(3)	0/43(0)	0/44(0)	3/40(8)	7/37(19)	2.7
Mo(98)	0/23(0)	0/23(0)	0/26(0)	1/39(3)	0/43(0)	40/44(91)	28/40(70)	9/37(24)	130
Rh(103)	0/23(0)	0/23(0)	1/26(4)	0/39(0)	0/43(0)	0/44(0)	1/40(3)	0/37(0)	1.7
Pd(105)	8/23(35)	2/23(9)	20/26(77)	30/39(77)	42/43(98)	5/44(11)	33/40(83)	31/37(84)	6.4
Ag(107)	2/23(9)	3/23(13)	7/26(27)	1/39(3)	2/43(5)	26/44(59)	4/40(10)	2/37(5)	7.7
Cd(114)	21/23(91)	21/23(91)	25/26(96)	37/39(95)	41/43(95)	43/44(98)	40/40(100)	37/37(100)	11
In(115)	0/23(0)	0/23(0)	0/26(0)	3/39(8)	5/43(12)	3/44(7)	35/40(88)	18/37(49)	3.9
Sn(118)	9/23(39)	14/23(61)	21/26(81)	33/39(85)	27/43(63)	36/44(82)	25/40(63)	24/37(65)	86

Table 1 (continued)

Element (m/z)	*Cerebrum white matter*	*Cerebrum grey matter*	*Cerebellum*	*Heart*	*Spleen*	*Liver*	*Kidney cortex*	*Kidney medulla*	*LLD*[a]
Sb(121)	0/23(0)	0/23(0)	0/26(0)	2/39(5)	0/43(0)	0/44(0)	0/44(0)	0/37(0)	6.6
Te(130)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	1/43(2)	0/44(0)	10/40(25)	11/37(30)	12
Cs(133)	10/23(43)	5/23(22)	23/26(88)	35/39(90)	39/43(91)	38/44(86)	34/40(85)	30/37(81)	1.7
Ba(138)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	1/43(2)	0/44(0)	0/40(0)	0/37(0)	470
La(139)	1/23(4)	0/23(0)	1/26(4)	2/39(5)	3/43(7)	26/44(59)	2/40(5)	1/37(3)	15
Ce(140)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	1/43(2)	2/44(5)	2/40(5)	1/37(3)	120
Pr(141)	0/23(0)	0/23(0)	1/26(4)	0/39(0)	1/43(2)	4/44(9)	2/40(5)	1/37(3)	6.4
Nd(146)	0/23(0)	0/23(0)	1/26(4)	0/39(0)	1/43(2)	4/44(9)	2/40(5)	1/37(3)	20
Sm(149)	0/23(0)	0/23(0)	1/26(4)	0/39(0)	0/43(0)	1/44(2)	1/40(3)	1/37(3)	6.6
Eu(153)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	1/43(2)	0/44(0)	1/40(3)	4/37(11)	0.7
Gd(157)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	0/43(0)	2/44(5)	2/40(5)	1/37(3)	7.4
Tb(159)	0/23(0)	0/23(0)	1/26(4)	0/39(0)	0/43(0)	2/44(5)	2/40(5)	1/37(3)	0.7
Dy(163)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	0/43(0)	0/44(0)	1/40(3)	0/37(0)	4.2
Ho(165)	0/23(0)	0/23(0)	1/26(4)	0/39(0)	0/43(0)	0/44(0)	1/40(3)	1/37(3)	0.8
Er(166)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	0/43(0)	0/44(0)	2/40(5)	2/37(5)	1.4
Tm(169)	0/23(0)	0/23(0)	1/26(4)	0/39(0)	0/43(0)	1/44(2)	1/40(3)	0/37(0)	0.5
Yb(172)	0/23(0)	2/23(9)	0/26(0)	0/39(0)	0/43(0)	2/44(5)	1/40(3)	0/37(0)	2.4
Lu(175)	0/23(0)	0/23(0)	0/26(0)	0/39(0)	0/43(0)	0/44(0)	1/40(3)	0/37(0)	1.6
Hf(180)	0/23(0)	0/23(0)	0/26(0)	1/39(3)	0/43(0)	1/44(2)	1/40(3)	1/37(3)	6.4
Ta(181)	2/23(9)	1/23(4)	1/26(4)	5/39(13)	9/43(21)	40/44(91)	2/40(5)	6/37(16)	1.4
W(184)	1/23(4)	0/23(0)	0/26(0)	0/39(0)	1/43(2)	1/44(2)	1/40(3)	0/37(0)	9.8
Re(185)	0/23(0)	0/23(0)	0/26(0)	1/39(3)	0/43(0)	0/44(0)	8/40(20)	0/37(0)	3.0
Pt(195)	0/23(0)	0/23(0)	0/26(0)	2/39(5)	1/43(2)	1/44(2)	3/40(8)	2/37(5)	27
Au(197)	20/23(87)	6/23(26)	14/26(54)	23/39(59)	26/43(60)	20/44(45)	25/40(63)	22/37(59)	2.0
Hg(202)	0/23(0)	0/23(0)	2/26(8)	3/39(8)	3/43(7)	34/44(77)	18/40(45)	22/37(59)	94
Tl(205)	5/23(22)	7/23(30)	10/26(38)	26/39(67)	19/43(44)	21/44(48)	19/40(48)	11/37(30)	0.6
Pb(208)	1/23(4)	1/22(4)	1/26(4)	0/39(0)	4/43(9)	11/44(25)	7/40(18)	1/37(3)	97
Bi(209)	1/23(4)	7/23(30)	0/26(0)	0/39(0)	0/43(0)	5/44(11)	7/40(18)	9/37(24)	3.7
Th(232)	NA	NA	1/26(4)	3/39(8)	1/43(2)	NA	1/40(3)	1/37(3)	2.6
U(238)	NA	NA	0/26(0)	0/39(0)	0/43(0)	NA	1/40(3)	1/37(3)	1.4

[a]Lower limit of determination expressed in ng/g wet organ weight. LLD was calculated using blank mean + 3SD and the average sample weight used in the present analysis (0.5 g) to show the order of the magnitude of the detection.

[b]Number of the sample with the concentration above LLD/number of sample analyzed. Percentage of the sample above LLD was in the parenthesis.

[c]Not analyzed.

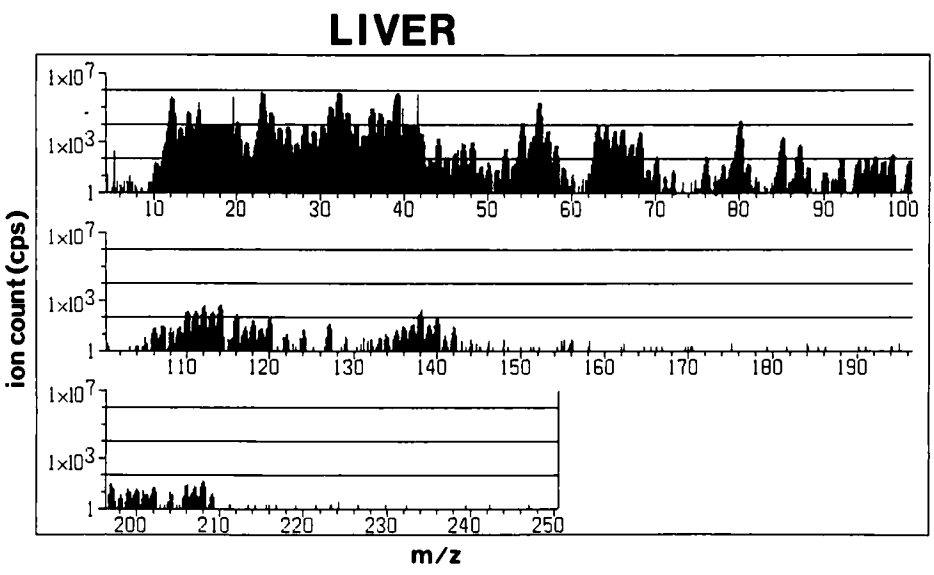

Figure 1 Mass spectrum of liver sample obtained by ICP-MS. Vertical and horizontal axis represents ion count (count per second, cps) and m/z, respectively.

RESULTS

Mass spectra of samples were obtained by the use of qualitative analysis mode and the result of liver sample is shown in Figure 1. Since 100 counts per second (cps, vertical axis) correspond approximately to 1 ng of the elements in 1 ml of sample solution, this figure also provides semi-quantitative information.

Table 1 presents the lower limit of determination (LLD) for all the elements analyzed, number of samples analyzed for each organ, and number of samples with the concentration above LLD. The LLD was defined as mean +3SD of the acid blank (number of analyses: 5). The weight of the sample for analysis varied from 0.1 to 1.4 g, therefore, LLD expressed on unit organ weight (g) basis was not consistent depending on the weight of the samples; LLDs given in Table 1 are those calculated for the sample of 0.5 g wet weight to show the order of the magnitude of detection. Since we used semiconductor-use nitric acid without further purification and PTFE-lined stainless-steel "bomb" for the sample digestion, we faced to a severe contamination problem, which practically determined the LLD.

Iron, Se, Sr, Pd, Sn, Cs, Au and Tl were the elements frequently detected regardless of the type of organs. Some elements were detected in the specific organs; Mn in spleen, liver and kidney, Mo, Hg and In in liver and kidney, and La in liver. The rate of the detection was low for Be in kidney and Ge in cerebrum when compared with other organs. The concentration of other elements, such as Li, Al, V, Co, Ni, Cr, Ga and lanthanides, was hardly above LLD in the samples of any organs.

Table 2 presents median elemental concentrations in Japanese organs expressed

Table 2 Elemental concentrations in organs determined by ICP-MS (wet weight basis)

Element (*m/z*)	*Unit*	*Cerebrum*		*Cerebellum(26)*	*Heart(39)*	*Spleen(43)*	*Liver(44)*	*Kidney*	
		White matter(23)[a]	*Grey matter(23)*					*Cortex(40)*	*Medulla(37)*
Li(7)	ng/g	—[b]	—	—	—	—	—	—	ND(ND–26.1)
Be(9)	ng/g	9.80(ND[c]–31.4)	ND(ND–11.2)	4.21(ND–11.4)	3.90(ND–111)	ND(ND–30.5)	ND(ND–22.3)	—	ND(ND–8.75)
Na(23)	μg/g	NA[d]	NA	187(53–407)	183(ND–540)	212(60–425)	NA	743(227–1720)	815(100–1860)
Mg(24)	μg/g	NA	NA	169(96–310)	250(72–376)	163(88–244)	NA	205(120–396)	178(101–301)
Al(27)	μg/g	ND(ND–3.67)	—	—	ND(ND–3.36)	—	ND(ND–2.55)	ND(ND–2.31)	—
Sc(45)	ng/g	546(205–1405)	270(43–679)	362(135–786)	480(300–1760)	269(171–799)	243(103–1140)	178(72–389)	125(48–433)
Ti(47)	μg/g	27.0(12.1–66.8)	18.9(11.3–42.4)	31.9(21.3–58.9)	22.9(12.8–31.7)	24.2(12.1–44.0)	20.3(10.1–35.8)	11.3(6.7–20.2)	7.8(4.1–13.7)
V(51)	ng/g	—	—	—	—	—	ND(ND–15.3)	ND(ND–577)	—
Cr(53)	μg/g	—	—	—	—	—	—	ND(ND–63.4)	—
Mn(55)	ng/g	ND(ND–524)	—	ND(ND–632)	ND(ND–640)	1232(ND–3680)	1380(ND–3030)	1050(ND–4790)	ND(ND–2330)
Fe(57)	μg/g	NA	NA	28.6(ND–84.7)	39.1(ND–94.5)	272(57–731)	NA	63.8(ND–783)	50.0(ND–364)
Co(59)	ng/g	—	—	—	—	—	ND(ND–56.7)	ND(ND–66.6)	—
Ni(60)	μg/g	—	—	—	—	—	—	ND(ND–9.23)	—
Cu(63)	μg/g	NA	NA	4.79(ND–11.5)	ND(ND–4.16)	ND(ND–1.48)	NA	ND(ND–19.3)	ND(ND–17.9)
Zn(66)	μg/g	NA	NA	11.9(8.5–21.4)	30.9(17.5–38.6)	17.8(8.6–25.0)	NA	72.6(24.5–137)	42.9(10.4–109)
Ga(69)	ng/g	—	—	—	—	—	—	—	—
Ge(72)	ng/g	ND(ND–54.1)	ND(ND–57.7)	ND(ND–37.7)	43.7(ND–138)	180(51–591)	78.4(ND–220)	35.3(ND–234)	19.8(ND–199)
As(75)	ng/g	ND(ND–175)	ND(ND–12.1)	ND(ND–15.1)	ND(ND–155)	ND(ND–53.5)	10.6(ND–183)	51.3(ND–163)	17.3(ND–93.9)
Se(82)	ng/g	ND(ND–314)	164(ND–310)	110(ND–327)	259(ND–615)	281(ND–511)	450(113–1320)	827(226–4685)	518(132–9220)
Rb(85)	μg/g	1.64(0.78–3.93)	1.88(1.15–3.94)	2.12(0.80–3.77)	2.99(0.31–5.34)	2.29(0.52–6.39)	3.86(0.29–9.10)	2.63(0.27–5.32)	2.47(0.27–5.21)
Sr(88)	ng/g	ND(ND–244)	ND(ND–328)	18.5(ND–59.7)	39.3(ND–168)	44.8(ND–435)	ND(ND–103)	88.0(26.5–545)	51.4(ND–259)
Y(89)	ng/g	—	—	—	ND(ND–15.5)	ND(ND–27.8)	ND(ND–46.8)	ND(ND–8.57)	ND(ND–5.91)
Zr(90)	ng/g	ND(ND–458)	—	ND(ND–86.1)	ND(ND–247)	ND(ND–222)	ND(ND–553)	ND(ND–374)	ND(ND–171)
Nb(93)	ng/g	—	—	—	ND(ND–5.49)	—	—	ND(ND–13.1)	ND(ND–13.4)
Mo(98)	ng/g	—	—	—	ND(ND–42.4)	—	853(ND–3090)	258(ND–12 400)	ND(ND–1232)
Rh(103)	ng/g	—	—	ND(ND–0.64)	—	—	—	ND(ND–1.11)	—
Pd(105)	ng/g	ND(ND–120)	ND(ND–95.9)	13.5(ND–81.0)	14.7(ND–105)	31.5(ND–100)	ND(ND–95.8)	25.1(ND–117)	24.0(ND–75.9)
Ag(107)	ng/g	ND(ND–20.6)	ND(ND–46.0)	ND(ND–63.0)	ND(ND–5.49)	ND(ND–15.1)	11.2(ND–1265)	ND(ND–15.2)	ND(ND–11.6)
Cd(114)	ng/g	66.2(ND–287)	86.9(ND–433)	49.9(ND–245)	112(ND–562)	535(ND–4030)	3.68(ND–98.6)[e]	73.3(0.018–335)[e]	32.2(0.009–187)[e]
In(115)	ng/g	—	—	—	ND(ND–47.1)	ND(ND–156)	ND(ND–10.6)	10.9(ND–47.5)	ND(ND–28.0)
Sn(118)	ng/g	ND(ND–430)	139(ND–1033)	133(ND–325)	202(ND–12 800)	110(ND–1940)	247(ND–1110)	115(ND–627)	122(ND–929)

Sb(121)	ng/g	—	—	—	ND(ND–60.4)	—	—	ND(ND–11.2)	—
Te(130)	ng/g	—	—	—	—	ND(ND–10.7)	—	ND(ND–62.6)	ND(ND–84.3)
Cs(133)	ng/g	ND(ND–7.48)	ND(ND–6.64)	3.99(ND – 11.5)	8.84(ND–27.5)	6.09(ND–19.9)	7.25(ND–22.3)	7.67(ND–25.8)	7.49(ND–28.0)
Ba(138)	ng/g	—	—	—	—	ND(ND–942)	—	—	—
LA(139)	ng/g	ND(ND–25.7)	—	ND(ND–21.5)	ND(ND–14.4)	ND(ND–160)	29.5(ND–118)	ND(ND–5265)	ND(ND–5733)
Ce(140)	ng/g	—	—	—	—	ND(ND–195)	ND(ND–103)	ND(ND–1793)	ND(ND–1851)
Pr(141)	ng/g	—	—	ND(ND–5.02)	—	ND(ND–15.0)	ND(ND–9.98)	ND(ND–410)	ND(ND–457)
Nd(146)	ng/g	—	—	ND(ND–15.6)	—	ND(ND–43.3)	ND(ND–28.4)	ND(ND–1020)	ND(ND–954)
Sm(149)	ng/g	—	—	ND(ND–63.8)	—	—	ND(ND–16.2)	ND(ND–30.9)	ND(ND–37.5)
Eu(153)	ng/g	—	—	—	—	ND(ND–1.42)	—	ND(ND–2.72)	ND(ND–4.05)
Gd(157)	ng/g	—	—	—	—	—	ND(ND–7.01)	ND(ND–180)	ND(ND–182)
Tb(159)	ng/g	—	—	ND(ND–1.92)	—	—	ND(ND–1.55)	ND(ND–9.35)	ND(ND–8.02)
Dy(163)	ng/g	—	—	—	—	—	—	ND(ND–5.94)	—
Ho(165)	ng/g	—	—	ND(ND–3.72)	—	—	—	ND(ND–19.9)	ND(ND–1.76)
Er(166)	ng/g	—	—	—	—	—	—	ND(ND–12.8)	ND(ND–10.4)
Tm(169)	ng/g	—	—	ND(ND–2.44)	—	—	ND(ND–0.34)	ND(ND–10.6)	—
Yb(172)	ng/g	—	ND(ND–9.55)	—	—	—	ND(ND–9.85)	ND(ND–7.82)	—
Lu(175)	ng/g	—	—	—	—	—	—	ND(ND–9.00)	—
Hf(180)	ng/g	—	—	—	ND(ND–12.7)	—	ND(ND–5.84)	ND(ND–18.7)	ND(ND–3.97)
Ta(181)	ng/g	ND(ND—7.28)	ND(ND–3.10)	ND(ND–2.36)	ND(ND–2.57)	ND(ND–4.64)	ND(ND–11.7)	ND(ND–1.31)	ND(ND–4.21)
W(184)	ng/g	ND(ND–76.2)	—	—	—	ND(ND–14.7)	ND(ND–41.2)	ND(ND–46.2)	—
Re(185)	ng/g	—	—	—	ND(ND–4.72)	—	—	ND(ND–60.3)	—
Pt(195)	ng/g	—	—	—	ND(ND–316)	ND(ND–320)	ND(ND–1170)	ND(ND–330)	ND(ND–145)
Au(197)	ng/g	10.8(ND–563)	ND(ND–12.4)	2.51(ND–22.9)	2.44(ND–656)	3.47(ND–79.6)	ND(ND–551)	3.18(ND–393)	2.98(ND–135)
Hg(202)	ng/g	—	—	ND(ND–138)	ND(ND–82.7)	ND(ND–248)	259(ND–2440)	ND(ND–6560)	249(ND–11 500)
Tl(205)	ng/g	ND(ND–3.84)	ND(ND–90.9)	ND(ND–1.58)	1.38(ND–6.95)	ND(ND–3.23)	ND(ND–4.84)	1.28(ND–9.66)	0.80(ND–9.05)
Pb(208)	ng/g	ND(ND–744)	ND(ND–8280)	ND(ND–151)	—	ND(ND–463)	ND(ND–2420)	ND(ND–1580)	ND(ND–4564)
Bi(209)	ng/g	ND(ND–17.9)	ND(ND–113)	—	—	—	ND(ND–704)	ND(ND–69.8)	ND(ND–124)
Th(232)	ng/g	NA	NA	ND(ND–5.93)	ND(ND–5.16)	ND(ND–12.4)	NA	ND(ND–3.30)	ND(ND–6.81)
U(238)	ng/g	NA	NA	—	—	—	NA	ND(ND–1.90)	ND(ND–10.6)

Figures in the table are median concentrations expressed on wet weight basis with min–max range in the parentheses..

[a]Number of samples analyzed in the parenthesis.

[b]None of the samples are above lower limit of determination (LLD, see Table 1).

[c]Below LLD.

[d]Not analyzed.

[e]Cd concentrations in liver and kidney are expressed in μg/g wet weight.

on wet weight basis, along with the minimum–maximum range. Sodium, Mg, Fe, Cu, Zn, Th and U in cerebrum and liver was not determined. The median, minimum or maximum value presented in the table is smaller than LLD given in Table 1 in some cases, because the LLDs are values for the samples with the average weight digested and the actual LLDs were lower than them in the samples with larger weight.

The following elements were determined by other analytical methods in the same organ sample, thus comparison of the analytical results by two methods could be undertaken: Na, Mg, Fe, Zn, Cd (ICP-AES), Se (fluorometry) and Hg (AAS). Comparison between the analytical results obtained by ICP-MS and those by ICP-AES was shown for Fe, Zn and Cd in Figures 2–4. Only the samples detected by both methods were plotted in the figures. Regression functions and correlation coefficients for these three elements were as follows: Fe: log Fe (AES) $=0.91\times\log$ Fe (MS) $+0.53$, $r=0.972$, $n=131$. Zn: log Zn (AES) $=0.94\times\log$ Zn(MS) $+0.21$, $r=0.982$, $n=184$. Cd: log Cd (AES) $=0.84\times\log$ Cd (MS) $+0.56$, $r=0.956$, $n=108$. Comparison was also conducted for Se (ICP-MS vs fluorometry) and Hg (ICP-MS vs AAS). Regression functions and correlation coefficients were as follows; Se; log Se (Flu) $=0.81\times\log$ Se (MS) $+1.44$, $r=0.889$, $n=243$. Hg: log Hg (AAS) $=0.85\times\log$ Hg (MS) $+1.29$, $r=0.833$, $n=70$. Correlation coefficients for these two elements were smaller than those for Fe, Zn or Cd. Regarding Na, comparison of the analytical results between ICP-AES and ICP-MS was not conducted because the discrepancy between the two was obvious, i.e., the range of Na concentrations in organs measured by ICP-AES was 1000–4500 μg/g[8], whereas the present result was several tens to 1800 μg.

DISCUSSION

Using qualitative analysis mode, ICP-MS provides qualitative as well as semi-quantitative information (Figure 1). Since ICP-MS is sensitive and its sensitivity is not so much different among the elements analyzed, one can easily identify which elements are contained in the sample. This feature seems to be quite important when unexpected toxic element(s) is contained in the sample.

Tables 1 and 2 provide quantitative information of elemental concentrations in human organs. At present, analytical data for Be, Rh, Pd, In, lanthanides, Hf, Ta, W, Re, Pt, Th concentrations in human organs or tissues are not available or are very limited in the literature. This group of elements includes those with toxicological importance or those to which human exposure is supposed to increase in the near future. With ICP-MS, as shown in Tables 1 and 2, it is possible to detect these elements in human organs. These tables also provide the organ-specific distribution of these elements. In general, liver and kidney concentrate many elements when compared with other organs. For instance, La was frequently detected in liver and In in kidney. The physiological or toxicological implication of the presence, organ levels and organ-specific distribution of the elements mentioned above must be clarified in future.

The following description deals with the problems of the present ICP-MS

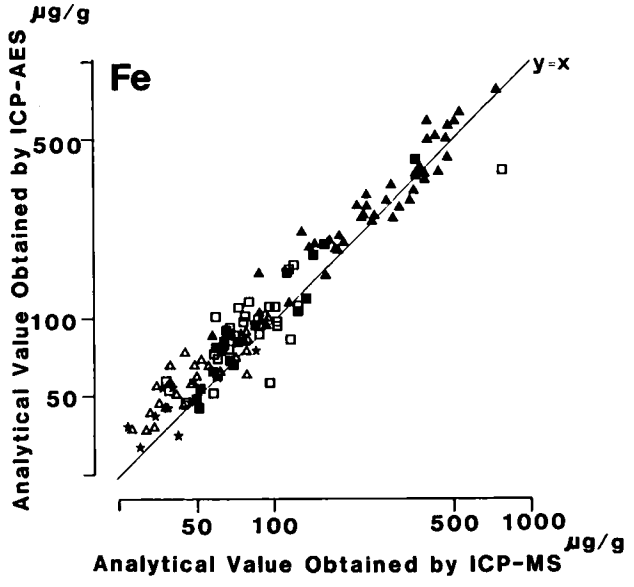

Figure 2 Comparison of the analytical values for Fe obtained by ICP-MS and those by ICP-AES. Log Fe (AES) = 0.91 × log Fe (MS) + 0.53, $r = 0.972$ ($p < 0.001$). Each symbol in the figure represents as follows; open square: kidney cortex, closed square: kidney medulla, open triangle: heart, closed triangle: spleen, closed star: cerebellum. Only the samples with detectable concentration by both of the analytical methods are plotted.

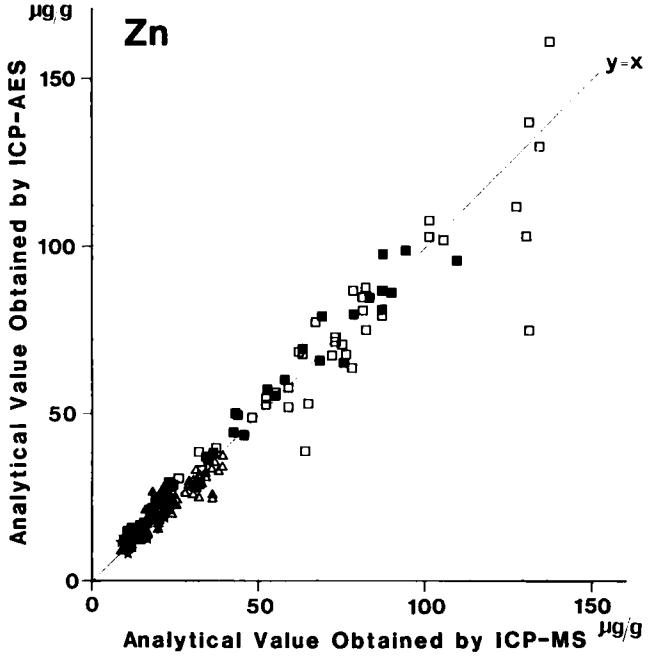

Figure 3 Comparison of the analytical values for Zn obtained by ICP-MS and those by ICP-AES. Log Zn (AES) = 0.94 × log Zn (MS) + 0.21, $r = 0.982$ ($p < 0.001$). Details are the same as those of Figure 2.

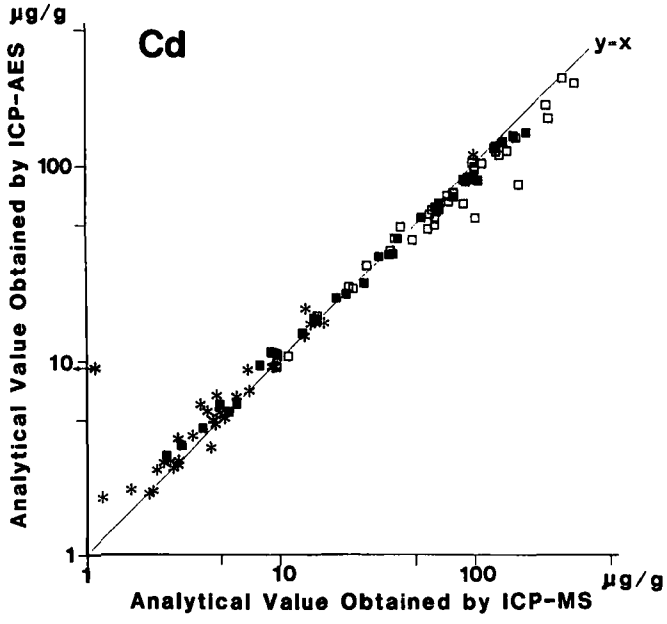

Figure 4 Comparison of the analytical values for Cd obtained by ICP-MS and those by ICP-AES. Log Cd (AES) = 0.84 × log Cd (MS) + 0.56, $r = 0.956$ ($p < 0.001$). Asterisk in the figure represents liver sample and other details are the same as those of Figure 2.

analysis, i.e., contamination and polyatomic molecular interference, and the validation of the present analytical data.

1. Contamination

The lower limits of determination for Na, Mg, Al, Cr, Mn, Fe, Ni, Cu, and Zn exceeded μg/g wet weight (Table 1). These values correspond to LLDs of several hundreds to several thousands ng/ml in sample solution. These high LLDs are due to the contamination from the acid and/or from the vessels used for sample digestion. The vessels used was of stainless-steel with PTFE-lining, thus traces of Fe, Ni, Cr or Zn might have leached into the sample solution. Sodium is one of the major contaminants of the commercial acid. During the multi-element analysis of human milk with ICP-MS,[9] we successfully lowered blank levels for these elements by the order of 1 to 3 (the maximum LLD, calculated by the same method as the present one, was 110 ng/ml for Na) using ultrapure nitric acid and inner-vessels made of PTFE for the digestion. Failed detection of Cr, Ni, Ba or Pb in most of the samples and frequent cases with below LLD for Mn, Fe or Cu are certainly due to high blank levels when compared with the previously reported organ content of these elements[8,10] with consideration of potential sensitivity of ICP-MS.

In contrast, the blank level of the elements with higher mass number were not so much lowered, and thus their LLDs were not lowered, by the use of ultrapure acid or PTFE inner-vessel as those for the elements mentioned above. Thus, failure of detection of the elements with higher mass number, such as lanthanides, in the present analysis is not due to contamination, but seems rather due to the lower levels in contemporary human organs.

2. Polyatomic Molecular Interference

Polyatomic molecular interferences were observed for several elements. Titanium was detected in all of the samples at the levels around 20 μg/g wet weight (Tables 1 and 2), but it was not detected by ICP-AES (LLD for Ti in 0.5 g organ was 1 μg/g wet weight). This implies that organ Ti levels obtained with ICP-MS (m/z 47) was overestimated probably due to polyatomic interference. One possible candidate for the inferference at m/z 47 is $^{31}P^{16}O$ since the organs contain P at the concentration of as high as 2000–3000 μg/g wet weight.[8] Scandium was detected at the levels of several hundred ng/g wet weight in most of the organ samples (Table 2). The present results are higher by the order of 1 to 3 than the previously reported values;[10] interference from unknown source at m/z 45 should be considered. Scandium is a monoisobaric element (^{45}Sc, 100%); hence this possible interference will be a critical problem for determination of Sc with ICP-MS. Organ Ge levels were sparsely reported, however, the present results (several tens to hundred ng/g wet weight, Table 2) may be overestimated by the interference at m/z 72 from iron oxide ($^{56}Fe^{16}O$). The use of m/z 74 may be recommended for Ge detection.

3. Validation of the Present Data

To examine the validity of the analytical results obtained from the present study, analysis of SRM and comparison of analyzed values obtained by the present method with those by other methods have been carried out. The results of the analysis of SRM revealed that analyzed values were fairly in good agreement with certified values for most of the elements measured for SRM, such as Na, Mn, Fe, Cu, Zn, Se, Rb, Sr, Mo, Ag, Cd, except for Mg and As, for which analyzed values were higher than certified values.[6] Interference of $^{40}Ar^{35}Cl$ might be attributed to the higher As value obtained, however, cause(s) of the discrepancy in Mg value were unknown. The results of the second validation method demonstrated good agreement for Fe, Zn and Cd between two methods, i.e., ICP-MS and ICP-AES (Figures 2–4). However, discrepancy was found for Na in addition to Mg. Since Na content of the organs, as determined by ICP-AES, were 2000–3000 μg/g wet weight,[8] it meant that sample solution contained about 100 μg Na/ml or more. The high Na content of the sample solution may be resulted in ion counting saturation, thus leading analyzed values to be lower. Relatively weaker correlation between the data obtained by ICP-MS and those by other methods for Se and Hg may be attributed in part to the vaporization of these elements during the sample preparation for ICP-MS analysis. For Se, in addition, mass number used for

Table 3 Validity of the results of the present ICP-MS analysis

Group 1	^{55}Mn, ^{57}Fe, ^{63}Cu, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{98}Mo, ^{107}Ag, ^{114}Cd, (^{23}Na)[a], (^{82}Se)[a]
Group 2	^{24}Mg, ^{45}Sc, ^{47}Ti, ^{72}Ge, ^{75}As, ^{202}Hg
Group 3	Others

Group 1: Element of which analytical result was validated through the analysis of Standard Reference Material (SRM, Bovine Liver, NBS 1577a) (Ref. 6) and/or comparison of the elemental concentration in organs determined by ICP-MS with those by other method.

Group 2: Element of which analytical result of SRM did not agree with the certified value and/or elemental concentration in organs determined by ICP-MS did not agree with those by other method or literature data.

Group 3 Element of which analytical result could not be validated by analysis of SRM and/or comparison with the other method. This group includes elements determined in the present study (see Table 1) excluding those in Groups 1 and 2.

[a]Result of SRM determination agreed with certified value, but comparison with the result of other method did not agree.

analysis was 82, which was an isotope with lower natural abundance (9.2%), to avoid major polyatomic interference resulting from $^{40}Ar^{40}Ar$ (^{80}Se, abundance: 49.8%) or $^{40}Ar^{38}Ar$ (^{78}Se, 23.5%). Further, interference at m/z 82 (CCl_2) is indicated in the multi-element analysis of clinical specimen with ICP-MS.[11] These factors can be involved in the discrepancies.

Table 3 summarizes the validity of the data obtained from the present ICP-MS analysis. There remains many elements to be validated and it will be done by use of other SRMs and/or the comparison with other analytical methods. Further validation of ICP-MS must be undertaken before this method contributes to the environmental sciences.

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