

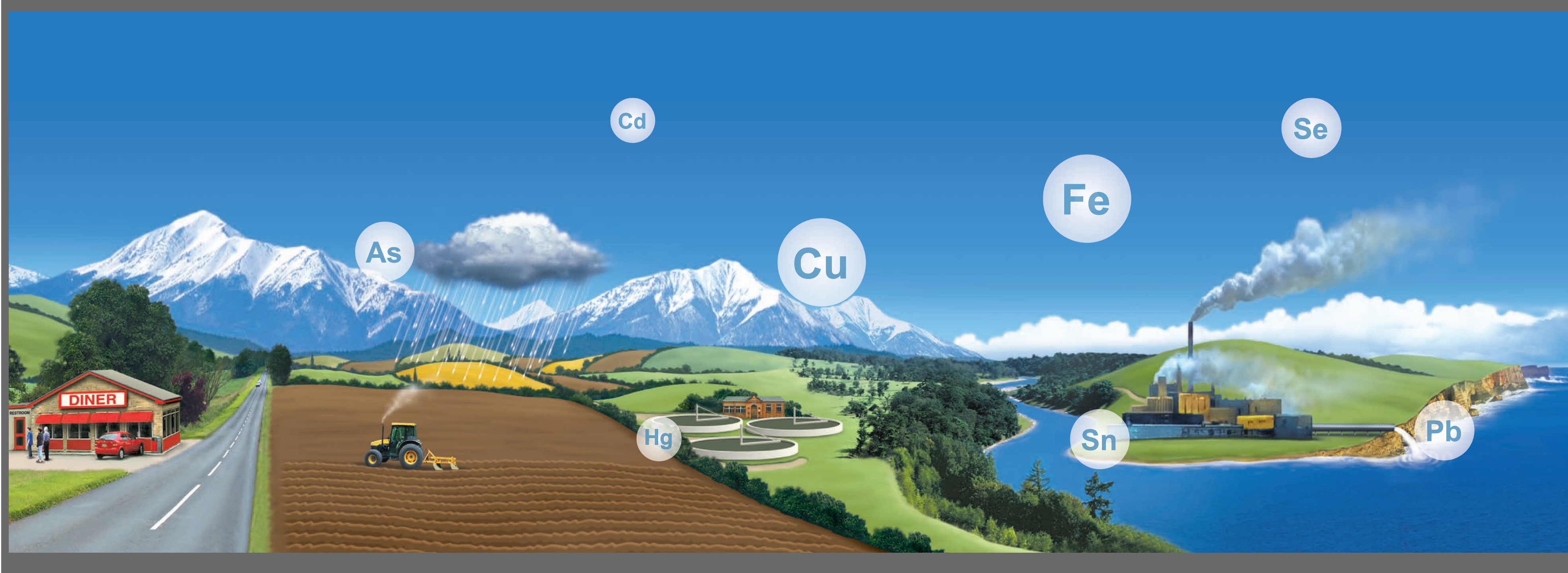
Trace Element Determination using ICP-MS for European Norms EN:DIN 15765 and 15763

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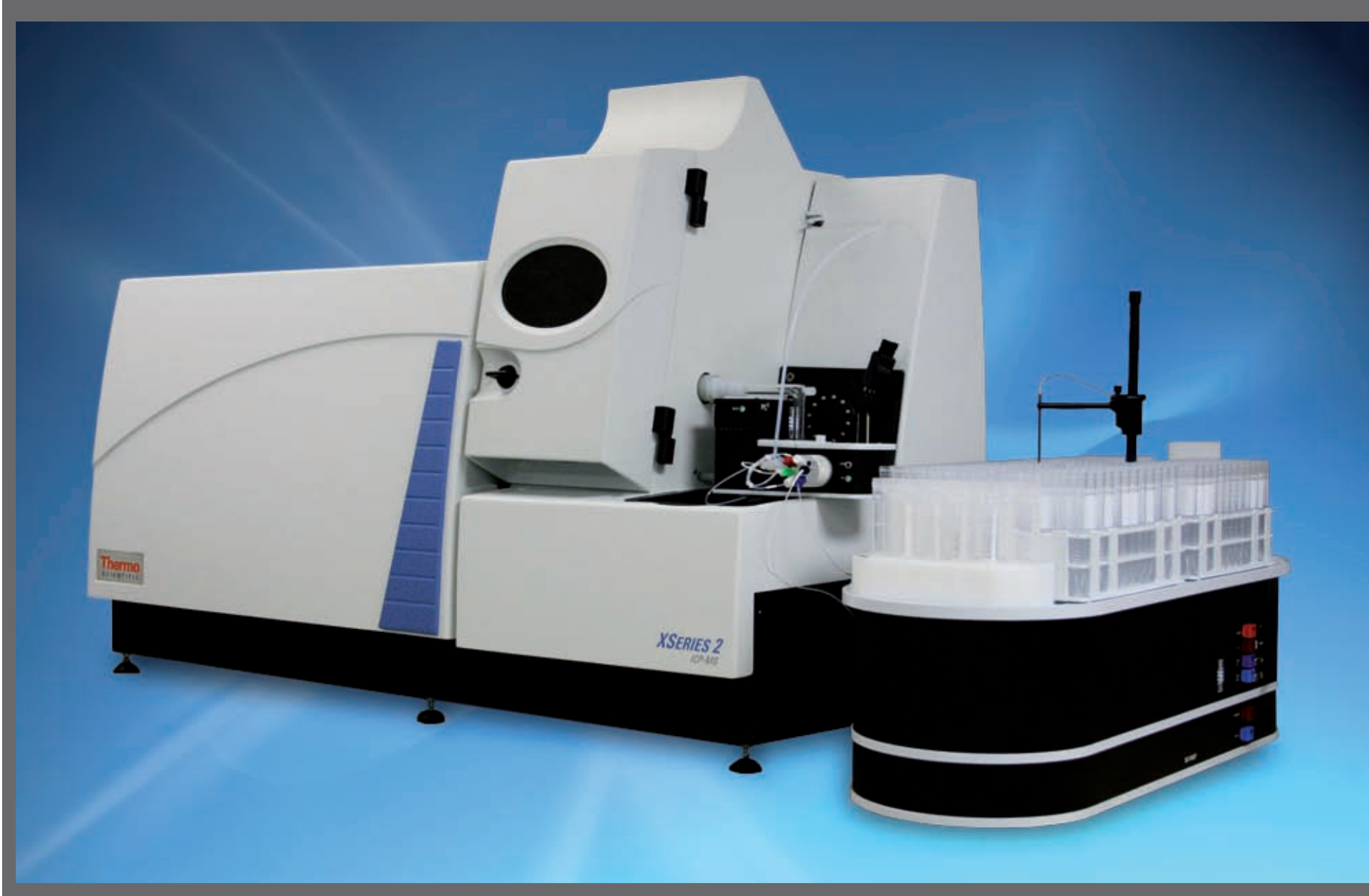
FIGURE 1. Trace elements and metals in our environment and food sources; which elements are present, in which matrices are they and how much is there?



Introduction

Food quality is promoted through consumer demand and food safety regulations. Trace elemental determination and in particular heavy metals in foods is a concern for the food safety community due to the potential toxicity of these metals.

FIGURE 2. Thermo Scientific XSERIES 2 ICP-Q-MS with ESI SC4 Autosampler and PC3 FAST



Worldwide, regulatory bodies for food safety stipulate upper limits for various elements. The most regulated elements/elemental species are arsenic (As), cadmium (Cd), mercury (Hg), lead (Pb) and inorganic tin (Sn).

European Norms, EN:DIN 15765 for Sn and EN:DIN 15763 for As, Cd, Hg and Pb address European Commission legislation (EC 1881/2006) and outline the sample preparation protocol based on microwave digestion (EN 13805) as well as the analytical procedure used for the metal quantification.

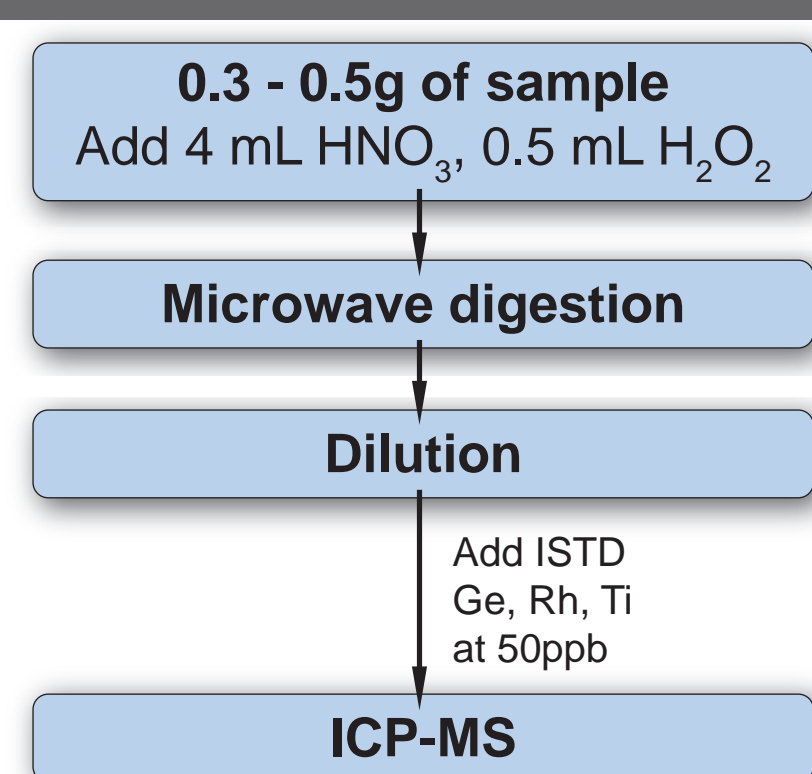
ICP-Q-MS is a sensitive, high throughput, fit-for-purpose tool for these methods. In addition to accurate and precise determination of the elements mentioned above, the multi-elemental nature of the instrumentation offers the potential to analyze a whole suite of elements in a single run. High linear dynamic range is another important feature that allows the determination of salt components (Na, K, P) in food and trace elements (Cd, Hg) simultaneously in one run.

Methods

The Thermo Scientific XSERIES 2 (Figure 2) used for quantification was operated in mixed-mode, that is to say with and without the use of the collision/reaction cell technology. The XSERIES 2 was configured with an SC4 PC3 FAST sample handling system from ESI (Elemental Scientific Inc., USA). The two European Norm protocols were used for a number of foodstuffs purchased from a local supermarket and four food matrix certified reference materials (CRMs). A simplified analytical methodology is illustrated in Figure 3. Triplicate microwave digests were prepared for each food and triplicate procedural blanks were prepared for each microwave batch.

External calibration was performed using multi-concentration, multi-elemental standards prepared from single element certified stock solutions. Samples were blank subtracted, quantified against the fully quantitative (FQ) calibrations and internal standard corrected. The measured concentration was then used to calculate the amount of each element in the original solid foodstuff.

FIGURE 3. Typical Sample Preparation for Metals in Foodstuffs



Results

Table 1 presents the data for the elements outlined in the EC regulation 1881/2006 and As for the four CRMs.

TABLE 1. Predicted fragments for the three phosphopeptides.

	NBS Bovine Liver		NIES 27 Japanese Diet		IRMM 804 Rice flour		DORM-3 Fish protein	
	Meas.	Cert.	Meas.	Cert.	Meas.	Cert.	Meas.	Cert.
As	0.047	0.047	0.575	0.600	0.040	0.049	6.47	6.88
Cd	0.421	0.440	0.064	0.069	1.517	1.610	0.299	0.290
Sn	0.0176		1.68	1.60			0.071	0.066
Hg	0.0036	0.0040	0.024		0.0037		0.376	0.382
Pb	0.126	0.135	0.603		0.400	0.420	0.393	0.395

Meas: Measured value calculated from FQ calibration and back calculated to the solid material according to sample weight taken for digestion and final dilution volume.
Cert: Certified value in mg / kg

Due to the multi-elemental capacity of ICP-MS, a number of other elements were simultaneously quantified. The high linear dynamic (LDR) range means that the major components of food, such as phosphorous (P), sodium (Na) and potassium (K) could be determined in the same run as the minor elements such as Cd and Hg. Figure 4 shows the coverage of the LDR where we see the calibration of K from 10 ppm to 0.2% and the calibration of Hg from 50 ppt to 10 ppb in the same run.

FIGURE 4. Fully Quantitative Calibration Curves for Potassium (K) from 10 to 2000 ppm and Mercury (Hg) from 0.05 to 10 ppb

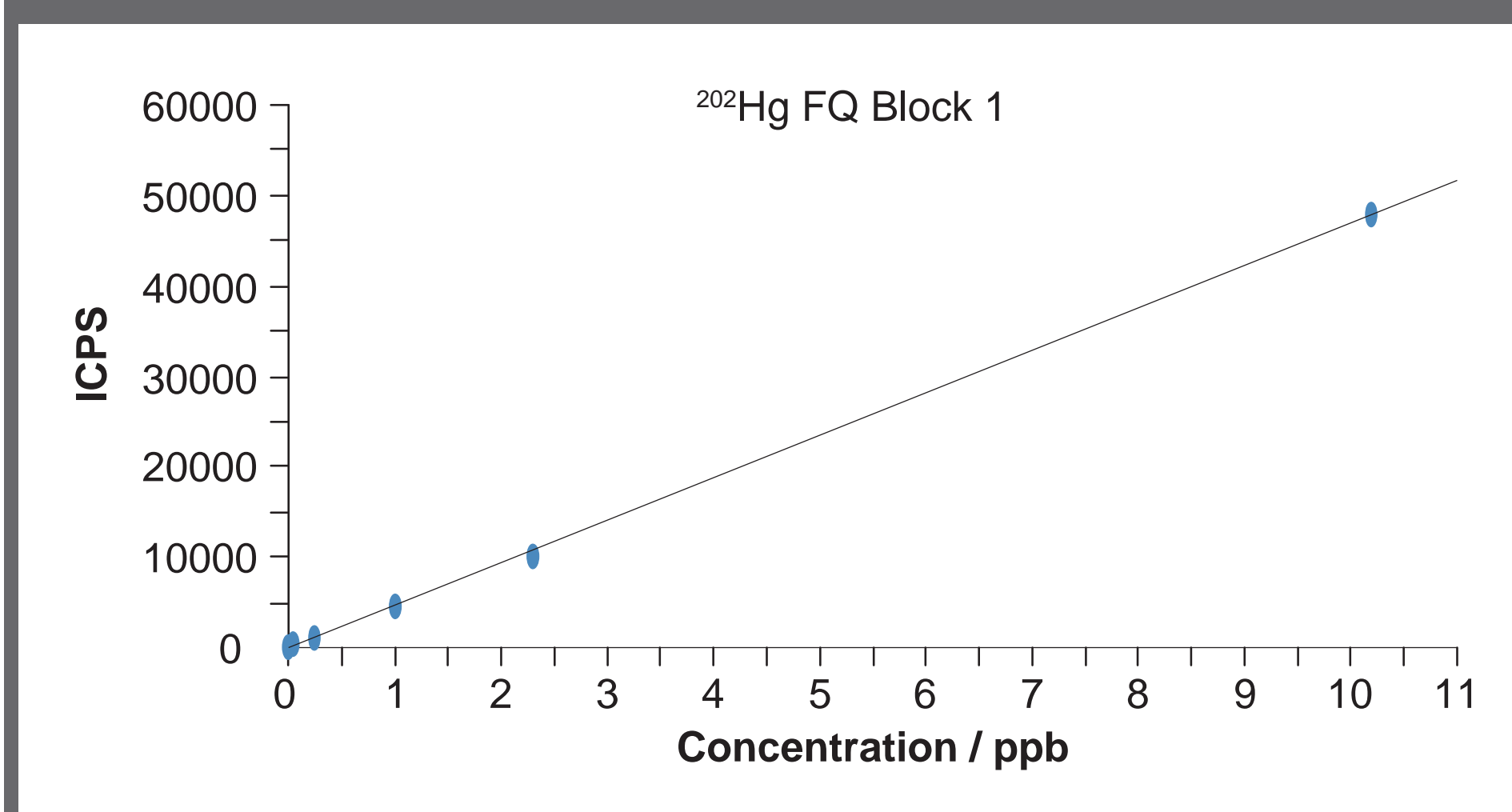
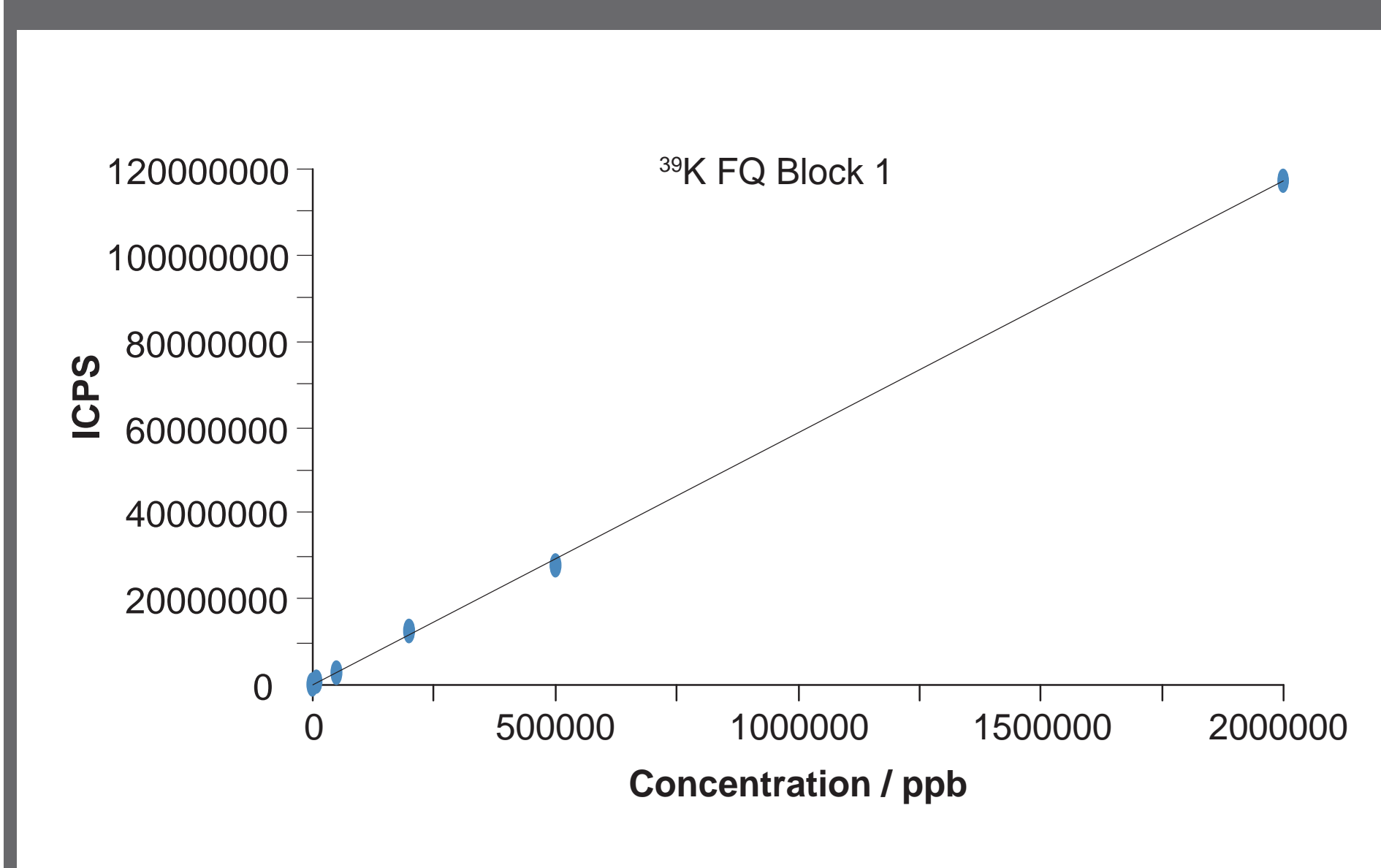


Table 2 shows the quantitative data for a larger number of analytes for two of the food CRMs. For all analytes, the measured and certified concentration where applicable are in good agreement. This demonstrates the power of ICP-MS to measure at sub-ppb level (Ag, Hg, U) whilst simultaneously measuring % level (Na, P, K). The data for a number of foodstuffs are shown in Table 3.

TABLE 2. Comparison of the Measured and Certified Concentrations in mg/kg and % (blue) for the two CRM materials

	NBS Bovine Liver		NIES 27 Japanese Diet	
	Measured	Certified	Measured	Certified
Na	0.26		1.02	1.00
Mg	628	600	612	576
Al	1.99		47.7	
P	1.05	1.11	0.24	
K	0.945	0.996	0.538	0.550
Ca	126	120	1357	1250
Mn	10.3	9.9	9.3	8.9
Fe	191	194	21	
Ni	0.490		0.491	
Cu	161	158	3.1	2.8
Zn	123	123	22.4	20.9
As	0.047	0.047	0.575	0.600
Se	0.72	0.71	0.24	0.25
Rb	11.9	12.5	4.39	
Sr	0.132	0.138	5.09	4.90
Mo	3.37	3.50	0.411	
Ag	0.0477	0.0400	0.0071	
Cd	0.421	0.440	0.064	0.069
Sn	0.0176		1.68	1.60
Ba	0.0749		1.18	1.10
Hg	0.0036	0.0040	0.024	
Pb	0.126	0.135	0.603	
U	0.00068	0.00071	0.0029	0.0029

TABLE 3. Quantitative Concentrations in mg/kg and % (blue) for Various Foodstuffs

	Prunes	Tinned tomatoes	Fenu-greek leaves	Hu-mous	White flour	Chilies	Cocoa	Rice	Sesame
Na	0,041	0,027	0,953	0,003	0,001	0,011	0,568	0,001	0,006
Mg	0,161	0,137	10,4	1,426	0,165	2,01	5,57	0,356	3,79
Al	2,94	2,28	1671	18,3	1,58	74,9	128	2,57	51,4
P	0,017	0,016	0,270	0,254	0,054	0,267	0,600	0,128	0,576
K	0,23	0,25	4,33	0,97	0,14	2,63	3,85	0,14	0,55
Ca	0,176	0,117	22,4	1,43	0,158	1,14	1,51	0,035	12,8
V	0,050	0,004	2,51	0,029	0,002	0,228	0,333	0,006	0,119
Cr	0,058	0,201	2,96	1,64	0,122	0,424	4,07	0,167	0,244
Mn	0,793	1,18	106	29,7	2,98	22,5	52,3	7,55	19,8
Fe	4,43	6,39	1236	59,1	7,86	118	356	4,76	112
Co	0,005	0,008	0,520	0,156	0,002	0,642	1,10	0,010	0,422
Ni	0,067	0,071	1,86	2,55	0,025	0,879	12,2	0,397	0,967
Cu	1,19	2,07	8,48	8,42	1,13	11,4	46,2	2,33	18,8
Zn	1,18	1,95	30,8	28,5	3,75	16,7	75,7	8,76	50,1
Ga	0,054	0,063	6,74	0,597	0,202	0,245	2,69	0,026	1,51
As	0,059	0,0004	0,610	0,017	0,0014	0,009	0,030	0,115	0,019
Se	0,0013	0,004	0,335	0,021	0,021	0,019	0,082	0,020	0,607
Rb	1,07	7,92	22,0	8,14	0,517	11,6	64,3	4,61	6,77
Sr	1,64	0,464	212	6,11	0,633	1,63	18,7	0,134	80,0
Mo	0,012	0,028	2,11	1,38	0,164	0,037	0,333	0,389	1,13
Ag	0,0008	nd	0,0265	0,0006	0,0007	0,0053	0,0030	0,0013	0,0043
Cd	0,0014	0,010	0,258	0,0025	0,021	0,063	0,137	0,033	0,017
Sn	0,065	47,2	0,133	0,013	0,000	0,003	0,012	0,0004	0,007
Ba	0,179	0,162	32,4	2,27	0,803	0,842	10,9	0,080	6,48
Hg	0,001	nd	0,021	0,0002	nd	0,0005	0,016	0,002	0,0003
Pb	0,024	0,040	1,06	0,020	0,0025	0,031	0,090	0,0027	0,035
U	0,033	0,0004	0,166	0,0003	nd	0,0012	0,0043	0,0006	0,0010

Conclusions

The results obtained for the CRMs were in very good agreement with the certified values, validating the method and the instrumentation for total elemental concentrations in foodstuffs. ICP-Q-MS is a fit-for-purpose tool for food safety and the determination of elements due to:

- High sensitivity
- High tolerance to matrix
- High linear dynamic range
- High throughput

The limits of detection (LODs) required for the EU Norms are shown in Table 4. The instrumental LODs, calculated from 3 blanks (3 x standard deviation) are well below the required LODs, demonstrating the suitability of this instrumentation and analytical approach for the determination of trace elements in food according to the EN Norms.

TABLE 4. Comparison of the instrumental limits of detection and the limits of detection required in the EN Norms 15763 and 15765.

Element	RLD	CLD
⁷⁵ As	0.5	0.049
¹¹¹ Cd	0.5	0.051
Sn	0.3*	0.015
²⁰² Hg	0.2	0.006
²⁰⁸ Pb	0.2	0.072

RLD: Required detection limit
CLD: Calculated detection limit of XSERIES 2 with SC4 FAST configuration

*The required detection limit of Sn has been estimated from a limit of quantification requirement of 1 ug/L Sn (no isotope specified) in EN15765