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Quantification of cadmium and lead in offal by SF-ICP-MS: Method development and uncertainty estimate

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Abstract

Offal of bovine, ovine and porcine are able to accumulate potentially toxic heavy metals, such as Cd and Pb, posing a risk for human health. For this reason, the Commission Regulation no. 466/2001 provided the maximum admitted levels for these metals in this kind of matrix (Cd, 500 ng g^{-1} in all kinds of offal; Pb, 500 ng g^{-1} in liver and 1000 ng g^{-1} in kidney). A method based on sector field inductively coupled plasma mass spectrometry for Cd and Pb quantification in calf liver was developed and further applied to offal of different animals. The uncertainty of measurements was calculated according to the Eurachem/Citac Guide. The method LoDs and LoQs were 3.5 and 11 ng g^{-1} for Cd, and 2.0 and 6.0 ng g^{-1} for Pb. The repeatability and the intra-laboratory reproducibility showed relative standard deviations equal to 2.25% and 1.99% for Cd and 1.49% and 6.55% for Pb. Relative expanded uncertainties at the mean value in calf liver were 4.74% for Cd and 13.8% for Pb. In Italian offal the following concentration intervals were found (in ng g^{-1}): (i) Cd: calf, from <3.5 in spleen and lung to 96.4 in kidney; lamb, <3.5 in all offal; pig, 114 in liver and (ii) Pb: calf, from 4.03 in lung to 31.8 in liver; lamb, from 4.71 in heart to 279 in liver; pig, 9.19 in liver.
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Keywords: Cadmium; Lead; Offal; Sector field inductively coupled plasma mass spectrometry (SF-ICP-MS); Measurement uncertainty

1. Introduction

Industrial and agricultural processes have been largely responsible for environmental pollution with toxic metals such as cadmium (Cd) and lead (Pb). Cadmium is mainly used in smelting, refineries of ores, batteries, and it was found, as an impurity, in fertilizers with rising concern for human and animal health. It mainly accumulates in kidney leading to proteinuria with severe damage for this organ. A massive Cd exposure can cause problems at bones because of the reduced activity of the vitamin D and the consequent failure in the Ca absorption as well as at neurological level because of its capability to replace Zn as metallo-enzyme (FAO/WHO, no. 46, 2001). With reference to Pb, beside its use as additive in motor fuels, it is utilized in iron and steel production, copper smelting, water pipes, bullets, etc. with significant releases in the environment. The human toxicity of Pb is largely proved, in fact, it is able to bind the SH-group of the proteins making enzymes inactive or replace other ions in metabolic functions with adverse effects on heme biosynthesis, kidney, nervous and cardiovascular systems (FAO/WHO, no. 44, 2000).

Offal of animals, such as liver and kidney, accumulates Cd and Pb at concentration higher than in muscle and than in most other food. Different authors found incremented Cd and Pb levels in kidney and liver of animals grazing in industrial areas (Abou-Arab, 2001; Miranda, López-Alonso, Castillo, Hernández, & Benedito, 2005; Sedki, Lekouch, Gamon, & Pineau, 2003). This augmented level was ascribed to either pollution of soil and plant by wastewater or by deposition of particles emitted from fumes and

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blown by the wind. For this reason, consumers of offal containing high level of Cd and Pb were exposed to not negligible health risks. In this view, the Commission Regulation (CR) no. 466/2001 of March 8, 2001 (EC, 2001), provided the maximum admitted level (MAL) of the two elements in edible offal. In particular, a MAL of 0.5 mg/kg for Cd in offal of bovine, porcine, ovine and poultry, and of 0.5 mg/kg in liver and 1.0 mg/kg in kidney for Pb in the same categories of animals have been established. Although metal concentrations in offal of cattle have been measured in a variety of Countries (Coleman, Elder, Basu, & Koppenal, 1992; Jorhem, Slorach, Sundström, & Ohlin, 1991; López-Alonso et al., 2000; Niemi, Venäläinen, Hirvi, Hirn, & Karppanen, 1991; Salisbury, Chan, & Saschenbrecker, 1991), there are very few data for offal of animals farmed in Italy (Amodio-Cocchieri & Fiore, 1987). The previously cited works used atomic absorption spectrometry (AAS) as the quantification technique, only one study utilized differential pulse anodic stripping voltammetry (DPASV). In this study, the sector field inductively coupled plasma mass spectrometry (SF-ICP-MS), with its high sensitivity, large dynamic range, multielementarity, high sample throughput per day, was investigated for the purpose. Nevertheless, the adoption of important instrumentation became useful only when the produced data are associated to a high degree of quality. In this context, current recommendations (ISO 17025, 1999) underline the importance of planning a method validation procedure and identifying all the sources of uncertainties arising from the entire analytical procedure. The association of the results with their uncertainty allows the correct comparison of analytical data between different laboratories and the assessment of the method suitability for its intended purpose. Some texts well define the scaffold of the validation process, limits of detection and quantification, sensitivity, linearity, repeatability, reproducibility, trueness, robustness and uncertainties of measurements (AOAC, 1989; Eurachem, 1998; ISO 5725, 2004). The Eurachem/Citac (2000) guide provides examples on how identifying uncertainty sources and combining the relevant uncertainty contributions. Recently, the ISO/TS 21748 guide (2003) suggests to use experimental data from precision and trueness or recovery studies in the calculation of uncertainty. The application to real samples is the step next to the validation with the aim to give evidence that the developed method can be used in the laboratory for a certain amount of time without losing the adequate analytical performances.

In light of this, a method based on microwave (MW)-assisted acid digestion and SF-ICP-MS for Cd and Pb in offal was developed and the analytical performances were used to estimate the expanded uncertainties, following the recommendations given by the above mentioned guides. The method was then applied to different kinds of edible bovine, ovine and porcine offal. The obtained results were also discussed in order to contribute to the assessment of Cd and Pb contamination in offal available on the Italian market.

2. Materials and methods

2.1. Sample collection and preparation

The method was developed on calf liver. The same material was used for the quality control study. The method was applied on eight different varieties of offal, namely, spleen, lung and kidney of calf; kidney of pig; liver, lung, kidney and heart of lamb. All the specimens were purchased in different supermarkets in Rome. All the animals were of Italian farms and not over 1-year of age. Visible fat and connective tissue were removed and samples were homogenized in a turbo homogenizer HMHF (PBI International, Milan, Italy) and kept at −20 °C until the analysis.

Prior their digestion, samples were allowed to reach the room temperature and further sub-sampled. Calf liver was digested by MW-assisted acidic digestion in MW oven (MLS-1200, FKV, Sorisole, Bergamo, Italy). Aliquots of approximately 2 g were transferred into Teflon vessels and added with 6 ml of a 5:1 (v/v) mixture of *Superpure* 67% HNO_3 (ROMIL, Cambridge, UK) and *Suprapur* 30% H_2O_2 (Merck, Darmstadt, Germany). The MW irradiation programme consisted of four steps as follows: 10 min at 250 W, 5 min at 400 W, 5 min at 500 W and 5 min at 600 W. After cooling at room temperature, the digested sample solutions were quantitatively transferred into disposable flasks and diluted to ca. 17 g with high purity deionized water (EASY Pure system, Barnstead, Dubuque, USA). The final weight was corrected for the density of the digested solutions in order to take into account for their acidity. Procedural blanks, the Certified Reference Material (CRM) 185R Bovine Liver and the other kinds of offal, were prepared following the same procedure. The resulting digested solutions were stored at +4 °C until analyses. Calibrants and standards were daily prepared from single element stock solutions of Cd, In, Mo, Pb and Rh at 1000 µg ml^{-1} (Spex Industries, Edison, USA) by dilution with water. To avoid contamination, all sample manipulation took place in a Class-100 Clean room (TAMCO, Milan, Italy).

2.2. Sample analyses

Digested samples were diluted $1 + 3$ (v/v) with water before quantification. The SF-ICP-MS (Element, Thermo-Electron, Bremen, Germany) was characterised by double focusing reverse Nier–Johnson geometry and sampler and skimmer cones in Ni alloy. The instrument was equipped with a Meinhard nebulizer, a water cooled spray chamber (Scott-type) and a Guard Electrode device. The critical instrumental parameters, such as argon flow rates, torch position, lenses and radio frequency (RF) power were daily optimized so as to reach a signal for 1 µg l^{-1} of ^{115}In of >900,000 counts per second (cps), established as acceptance limit. Also the oxides formation was daily minimized on the BaO^+/Ba^+ ratio, usually maintained below 0.002. The final instrumental settings were as follows: RF generator, 1250 kW; plasma flow rate, 15 l min^{-1}; auxiliary and

sample gas flows ranged 0.8–1.0 l min^{-1}; sample flow rate, ca. 1.0 ml min^{-1}; temperature of the spray chamber, ca. 10 °C. The analytical masses ^{114}Cd, ^{115}In, ^{208}Pb were selected, and the Low Resolution (LR) mode ($m/\Delta m = 300$) was used to work at the maximum of instrumental sensitivity. The species ^{98}Mo^{16}O and ^{114}Sn were checked as potential interferences on the mass 114 but their contribution to the actual Cd signal (i.e., 0.2% of MoO and 0.4% of Sn) resulted to be negligible. The standard addition calibration approach was chosen so as to overcome matrix effects in SF-ICP-MS analysis. The internal standardization (IS, In at the concentration of 1 ng ml^{-1} in calibrants and samples) was applied to compensate for any random fluctuations of the signals. The intra-run signal stability was controlled by measuring a check sample (calf liver spiked with 1 ng ml^{-1} of Cd and Pb) and a maximum fluctuation of ±10% was accepted. Blanks were included in the analytical sequence to check for any signal contributions due to chemicals and ancillary equipments.

2.3. Analytical figures of merit

Calibrations curves on calf liver were constructed on at least five concentration levels and squared correlation coefficients (R^2) > 0.9990 were considered as acceptable. The *instrumental* Limit of Detection (LoD) was calculated as the concentration associated with 3.3-times the standard deviation (SD) of the background noise recorded on 10 independent measurements of the procedural blanks. The *method* LoD was analogously calculated, but with the real matrix. The *instrumental* and *method* Limits of Quantification (LoQs) were expressed as 10-times the SD on 10 replicated measurements of blanks or matrices, respectively. The sensitivity was evaluated on the basis of the slope of the calibration curve and expressed in cps for 0.25 ng ml^{-1} of Cd and Pb. The method linearity was measured on 11 different concentrations spanning the range 0.125–32 ng ml^{-1} for Cd and Pb and the R^2 was used as indicator of the linear relationship between signal and concentration. The trueness (%) is the difference between the certified and the found values divided for the certified one. Trueness was checked throughout the use of the CRM 185R Bovine Liver (IRMM, Geel, Belgium) where Cd and Pb have certified values of 544 ± 17 ng g^{-1} and 172 ± 9 ng g^{-1}, respectively, and it was calculated digesting three aliquots of the CRM on six different days for a total of 18 independent measurements. The repeatability was expressed as the relative (R)SD for a total of 21 independent samples analysed by the single analyst on three different days. The intra-laboratory reproducibility was the RSD of 21 independent samples analyzed on 3 days by changing the analyst, the instrumentation (second generation of the same technique, i.e. Element2), the pipettes and the batches of the stock standard solutions. The robustness of the method is the capability of tolerating small changes in parameters without affecting the analytical signal. To assess this characteristic, two series (seven independent samples each) of data,

one acquired with the original method and the other under slightly different instrumental working conditions, were compared. The variations to the method were: HNO$_3$ 65% of *Suprapur* grade from Merck, Darmstadt, Germany, sample flow rate of ca. 1.3 ml min^{-1}, Rh as the IS at the concentration of 1 ng ml^{-1}, spray chamber kept at room temperature. Results obtained were compared with the *t*-test on means and a *p* value of <0.05 was considered as significant.

2.4. Calculation of measurement uncertainty

In accordance to the recommendations from the Eurachem/Citac Guide (2000) and the ISO/TS 21748 (2003), the analytical figures obtained in this study were used to estimate the expanded uncertainties for Cd and Pb in offal by SF-ICP-MS. Since the applied procedure was the same for both calf liver and other offal samples, it was assumed that all the uncertainty sources were covered by the analysis of calf liver. In particular, the following sources of uncertainty were identified in the developed analytical protocol: the balance when weighting raw mass of liver and diluting the digested samples; the pipettes when preparing calibrants and standards; the purity of the stock standard solutions; the linearity of calibration; the reproducibility and the CRM measurements. On these bases, the single contributes to the overall uncertainty were: (1) the relative uncertainty of the balance (u_b) declared by the manufacturer and taken as a rectangular distribution, i.e. $u_b = \frac{RSD}{\sqrt{3}}$; it was accounted for twice, for each weighing (when weighing the raw mass and when diluting up to ca. 17 g); (2) the relative uncertainty of the stock standard solutions (u_{std}) given in the supplier's certificate and approximated to a rectangular distribution, i.e., $u_{std} = \frac{RSD}{\sqrt{3}}$; (3) the relative uncertainty of the reproducibility (u_{rep}) calculated as the RSD of the intra-laboratory reproducibility measurements; (4) the relative uncertainty of the CRM (u_{crm}) based on the triangular distribution, calculated as $u_{crm} = \frac{RSD}{\sqrt{6}}$. As regards the uncertainty on the pipettes, it can be neglected because during the reproducibility study different pipettes have been used. Also the uncertainty related to the calibration curve is not an additive source of uncertainty but it is included in the reproducibility factor. Thus, the relative combined uncertainty (u_{comb}) was calculated as the square sum of all the relative standard uncertainties following the equation: $u_{comb} = \sqrt{u_b^2 + u_{std}^2 + u_{rep}^2 + u_{crm}^2}$. Finally, the relative expanded uncertainty U was calculated by multiplying the u_{comb} with a coverage factor of 2 which gives an interval containing approximately 95% of the distribution of values.

3. Results and discussion

3.1. Method performances

In Table 1 the obtained data are reported in terms of instrumental and method LoD and LoQ, linearity range,

Table 1
Validation data

Parameters	Unit	Cd	Pb
Instrumental LoD	ng ml^{-1}	0.005	0.06
Instrumental LoQ	ng ml^{-1}	0.015	0.18
Method LoD	ng g^{-1}	3.50	2.00
Method LoQ	ng g^{-1}	10.8	6.00
Linearity range	ng ml^{-1}	0.125–32	0.125–32
Sensitivity	cps/0.25 ng ml^{-1}	26,253	166,752
Trueness ($n = 18$)	%	1.34	5.65
Repeatability (RSD) ($n = 21$)	%	2.25	1.49
Intra-laboratory reproducibility (RSD) ($n = 21$)	%	1.99	6.55

Table 2
Relative standard uncertainty budget for Cd and Pb in offal

Uncertainty components	Cd (%)	Pb (%)
u_b	0.43	0.43
u_{std}	0.12	0.12
u_{rep}	1.99	6.55
u_{crm}	1.27	2.14
u_{comb}	2.37	6.90
U	4.74	13.8

sensitivity, recovery, repeatability and intra-laboratory reproducibility. The LoDs and LoQs are expressed in ng of each element per ml of final diluted digested sample solution and per g of sample weight. The procedure reached adequate detection power to quantify the elements under study, because the *method* LoDs for both elements were about five-times lower than the concentration found in real samples. The LoD here obtained for Cd in matrix was comparable with that reported for DPASV and Zeeman electrothermal atomisation (Z-ETA)-AAS (López-Alonso et al., 2000; Niemi et al., 1991; Vos, Hovens, & van Delft, 1987) and better of that obtained by Salisbury et al. (1991) with the graphite furnace (GF)-AAS technique, i.e., 10 ng g^{-1}. For Pb, the LoD here found on calf liver was from 5- to 20-times lower than that reported in literature for DPASV (Vos et al., 1987), ZETA-AAS (López-Alonso et al., 2000; Niemi et al., 1991) and GF-AAS (Salisbury et al., 1991) techniques.

In each day of analysis calibration curves gave R^2 higher than to 0.9992 for both elements, linearity was of two orders of magnitude with R^2 equal to 0.9996 for Cd and to 0.9997 Pb over the tested concentration range. As concern the trueness study, the recovery was quantitative for both elements. In addition, the method showed a negligible measurements dispersion under repeatability conditions, in fact, for both element it was about 2%. When varying factors such as the operator and the instrument (i.e., during reproducibility conditions) a slightly higher variance was observed only for Pb. The robustness was calculated after changing four instrumental parameters: two of them can interfere with the sample introduction in the plasma, one can influence the correction of instrumental drifts and the last can affect blank levels. Because the final data did not statistically differ from one to another operative condition ($p > 0.1$ for both elements), it can be concluded that the selected variations did not introduce any worsening of the method performances.

3.2. Quantification of the uncertainty components

Four contributions to the total uncertainty of the proposed method have been taken into account, i.e., balance, stock standard solutions, intra-laboratory reproducibility and CRM. The size of the contributions of the different relative standard uncertainties were calculated and reported in Table 2. The results showed that the uncertainties related to u_b and u_{std} were small when compared with the others that it is clearly safe to neglect their role in the u_{comb}. For Cd, u_{rep} and u_{crm} contributed for the 50% each to the combined uncertainty, while in the case of Pb, the u_{rep} had the largest part in the uncertainty, being the 75% of the u_{comb}. As a conclusion, the u_{comb} of the described method was obtained by summing only u_{rep} and u_{crm}. Applying the coverage factor of 2, the U were 4.74% for Cd and 13.8% for Pb at the mean concentrations found in real samples.

3.3. Levels of Cd and Pb in offal

Different types of offal (liver, kidney, spleen, lung and hearth) in calf, pig and lamb were analyzed for Cd and Pb content using the method here developed. The levels found in calf, pig and lamb were reported in Tables 3–5, respectively. Due to the limited number of published papers in this field, values obtained in cattle and sheep were also used for comparison throughout the text. However, this comparison can be limited by the age of animals, which is not often reported precisely, since it is well-known that metals accumulate in organs according to the age.

As regards Cd in calf (see Table 3), it was found at higher concentration in kidney, at moderate level in liver, while fairly absent in spleen and lung. Data on calf liver appeared to be rather similar to those of other Countries (Larsen et al., 2002; Miranda et al., 2005; Salisbury et al., 1991), except for two cases, in USA and Spain, where the concentration was about three-times higher and seven-times lower, respectively (Coleman et al., 1992; López-Alonso et al., 2000). With reference to kidney, levels in calf from Spain were comparable to those here obtained, whereas other studies reported higher concentrations (Coleman et al., 1992; Larsen et al., 2002; Salisbury et al., 1991). The ratio of 2:1 between Cd in kidney and in liver observed in this study was also found by Coleman et al. (1992), while other authors reported kidney levels increased of ca. seven-fold respect to liver (López-Alonso et al., 2000; Salisbury et al., 1991). Cadmium concentration ranges in cattle liver, i.e., 56–120 ng g^{-1} (Abou-Arab, 2001; Amodio-Cocchieri et al., 1987; Doganoc, 1996; Falandysz,

Table 3
Mean concentration (in ng g^{-1}, w/w) of Cd and Pb in offal of calf compared with literature data

	Cd	Pb	Country	References
Liver	58.2 ± 1.8	31.8 ± 1.2	Italy	This work
	40 ± 60	100 ± 140	Canada	Salisbury et al. (1991)
	190 ± 160	840 ± 300	USA	Coleman et al. (1992)
	7.78[a] (<LoD–7990)	33.0[a] (<LoD–446)	Spain	López-Alonso et al. (2000)
	42 (7–188)	17 (<16–75)	Denmark	Larsen et al. (2002)
	22.9[a] (6.43–221)	20.7[a] (<LoD–174)	Spain	Miranda et al. (2005)
Kidney	96.4 ± 4.5	22.9 ± 1.3	Italy	This work
	260 ± 470	150 ± 180	Canada	Salisbury et al. (1991)
	360 ± 760	870 ± 430	USA	Coleman et al. (1992)
	54.3[a] (2.43–1302)	38.9[a] (<LoD–1152)	Spain	López-Alonso et al. (2000)
	198 (32–774)	53 (<16–102)	Denmark	Larsen et al. (2002)
	96.4[a] (4.20–454)	15.9[a] (<LoD–118)	Spain	Miranda et al. (2005)
Spleen	<3.5	4.26 ± 0.68	Italy	This work
Lung	<3.5	4.03 ± 0.58	Italy	This work

Range in brackets.
[a] Geometric mean.

Table 4
Mean concentration (in ng g^{-1}, w/w) of Cd and Pb in offal of pig compared with literature data

	Cd	Pb	Country	References
Liver	114 ± 9	9.19 ± 0.43	Italy	This work
	199 ± 122	357 ± 131	Italy	Amodio-Cocchieri and Fiore (1987)
	28 ± 17	38 ± 21	Finland	Niemi et al. (1991)
	19 ± 10	19 ± 24	Sweden	Jorhem et al. (1991)
	90 ± 60	70 ± 60	Canada	Salisbury et al. (1991)
	210 ± 140	700 ± 170	USA	Coleman et al. (1992)
	90 ± 60	60 ± 50	Slovenia	Doganoc (1996)
	42 (17–231)	<16 (<16–25)	Denmark	Larsen et al. (2002)

Range in brackets.

1993; Jorhem et al., 1991; Niemi et al., 1991; Vos et al., 1987) overlapped those found in calf, while ranges for cattle kidney moved to higher levels, i.e., 220–610 ng g^{-1} (Abou-Arab, 2001; Amodio-Cocchieri et al., 1987; Doganoc, 1996; Falandysz, 1993; Jorhem et al., 1991; Niemi et al., 1991; Vos et al., 1987), thus suggesting that Cd accumulates in kidney depending on the age of animal. As in the case of calf, in cattle Cd was higher in kidney than in liver. Despite our data suggested the absence of Cd in spleen and lung, relatively high levels, i.e., 90 ng g^{-1}, were found in cattle spleen farmed in Egypt (Abou-Arab, 2001) and in cattle lung from Eastern Europe, i.e., 20–330 ng g^{-1}, depending on the site (Farmer & Farmer, 2000). In pigs (see Table 4), Cd value in liver well matched with the one reported in another Italian study; among the other Countries, the lowest data were obtained in the northern part of Europe (Jorhem et al., 1991; Larsen et al., 2002; Niemi et al., 1991). In the case of lamb (see Table 5), Cd was below the LoD for all the offal samples. Other investigations (Coleman et al., 1992; Jorhem, 1999; Karavoltsos, Sakellari, Dimopulos, Dasenakis, & Scoullos, 2002; Reykdal & Thorlacius, 2001) quantified this element at the level of tenth of ng g^{-1} in both liver and kidney. In Italian lambs, Cd values up to 1 μg g^{-1} were detected in kidney

(Amodio-Cocchieri et al., 1987). This last author traced back the high values to the use of local forages for feeding animals containing a high Cd content. Both sheep and lamb accumulated Cd in liver (56–320 ng g^{-1}) at comparable levels (Abou-Arab, 2001; Falandysz, 1991; Vos, Lammers, & van Delft, 1988; Zantopoulos, Antonoiu, & Nikolaidis, 1999). On the contrary, the kidney of sheep (250–1230 ng g^{-1}) (Falandysz, 1991; Jorhem, 1999; Vos et al., 1988; Zantopoulos et al., 1999) presented higher Cd concentration than in lamb. Differently from the results of this study, other authors obtained Cd values from 80 to 180 ng g^{-1} in heart and lung of sheep (Abou-Arab, 2001; Farmer et al., 2000).

Lead was quantified in all the analyzed calf offal (see Table 3) ranging from 4.03 ng g^{-1} in lung to 31.8 ng g^{-1} in liver. Data in calf liver and kidney were close to each other and matched those reported in literature (Larsen et al., 2002; López-Alonso et al., 2000; Miranda et al., 2005; Salisbury et al., 1991), with the exception of Coleman et al. (1992), who found very high values in both organs. Another author (Abou-Arab, 2001) analysed spleen of bovine obtaining a value three-times higher than that found here. For cattle, the results on Pb were more or less similar to those in calves with equal accumulation

Table 5
Mean concentration (in ng g^{-1}, w/w) of Cd and Pb in offal of lamb compared with literature data

	Cd	Pb	Country	References
Liver	<3.5	279 ± 11	Italy	This work
	219 ± 109	537 ± 219	Italy	Amodio-Cocchieri and Fiore (1987)
	140 ± 50	710	USA	Coleman et al. (1992)
	31 ± 53	31 ± 21	Sweden	Jorhem (1999)
	45 ± 37	–	Iceland	Reykdal and Thorlacius (2001)
	16.3 ± 1.0	–	Greece	Karavoltsos et al. (2002)
Kidney	<3.5	172 ± 10	Italy	This work
	1035 ± 1005	696 ± 361	Italy	Amodio-Cocchieri and Fiore (1987)
	180 ± 100	640 ± 90	USA	Coleman et al. (1992)
	120 ± 270	53 ± 38	Sweden	Jorhem (1999)
	58 ± 50	–	Iceland	Reykdal and Thorlacius (2001)
	22.2 (medulla); 8.9 (cortex)	–	Greece	Karavoltsos et al. (2002)
Lung	<3.5	72.2 ± 2.7	Italy	This work
Heart	<3.5	4.71 ± 0.14	Italy	This work

in liver and kidney (Abou-Arab, 2001; Doganoc, 1996; Falandysz, 1993; Jorhem et al., 1991; Niemi et al., 1991; Vos et al., 1987). In Italian beef, Pb values were higher in both organs (Amodio-Cocchieri et al., 1987). In this context, the data obtained in the last two decades for Pb in calf or cattle showed a decrease in the element concentration in both liver and kidney (see Fig. 1). In particular, in Italy, from 1987 to 2006 Pb values have been lowered 12-times, while, from 2000 till now, data were rather homogeneous. The decrement might be traced back in the restriction of the use of this metal in fuel (Miranda et al., 2005) or in the improvement of the analytical quality control system (Jorhem, 1999). In pigs (see Table 4), a very low Pb value, comparable with the data obtained in Denmark and Sweden (Jorhem, 1991; Larsen et al., 2002),

was found in liver. In Italy and USA values in pigs were much higher (Amodio-Cocchieri et al., 1987; Coleman et al., 1992). When offal of lamb was considered, as reported in Table 5, Pb accumulated in liver and kidney more than in lung and heart. Once more, the works of Amodio-Cocchieri et al. (1987) and Coleman et al. (1992) found a higher Pb content in both organs. Considering data for liver and kidney of sheep, Vos et al. (1988) and Zantopoulos et al. (1999) supplied much higher concentrations (with a maximum of 960 ng g^{-1} for both organs) than those here reported for lamb, whereas Falandysz (1993) and Abou-Arab (2001) found similar data. In addition, Pb level in heart and lung given by literature was higher than the level found in this work (Abou-Arab, 2001; Farmer et al., 2000).
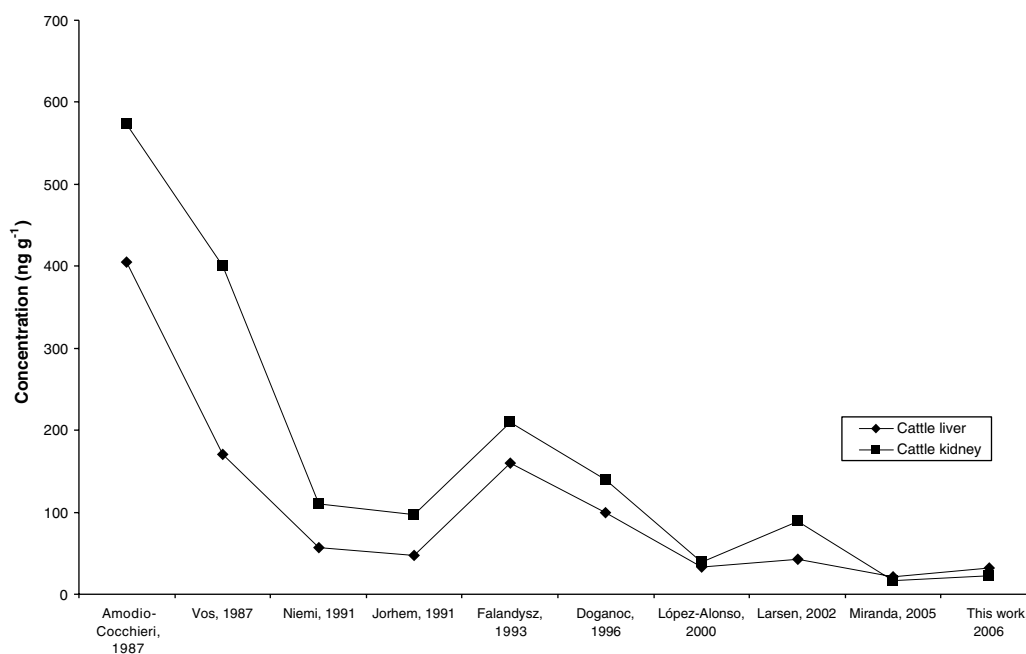

Fig. 1. Trend of Pb level in bovine kidney and liver over two decades.

In summary, results for Cd indicated that kidney and, to a lesser extent, liver are the critical organs for accumulation of this element. This result had been foreseen since the Cd elimination rate from these two organs is relatively low, partly due to the link with metallothioneins in these tissues. Cadmium levels in lung, spleen and heart were below the LoD in all the animals analyzed. Data of Cd in calves appeared to be lower than those in cattle reported in literature and this fact can be easily attributed to the young age of the animals. Lead appeared to accumulate with the same concentration in kidney and liver, while levels in lung, spleen and heart were lower. Moreover, the Pb concentration in offal of lamb was higher than the one in calf and pig. This could be due to the fact that lambs were more prone to Pb contamination due to their grazing outside, on the contrary, calves and pigs are fed indoors. In comparison with literature, Cd and Pb levels appeared to be amongst the lowest recorded in Europe, Canada and USA. In this frame, it has been reported that most of the Italian unpolluted cultivated soil are alkaline or sub-alkaline. This fact makes the Cd and Pb bio-availability from soil very low, limiting their absorption from plant used for forages (Ferraresi & Corticelli, 2002).

4. Conclusions

An analytical approach for the determination of Cd and Pb in offal samples by SF-ICP-MS, based on the evaluation of a number of method's parameters, is described. In addition, the data were then used for the uncertainty assessment. The total uncertainty of the method was composed mainly from the contribution of the intra-laboratory reproducibility, while some sources of uncertainty were neglected. Values obtained for Cd and Pb in offal from different animals were below the maximum admitted level for these elements in edible offal and well matched with those present in literature. These results are much in a preliminary phase and have to be confirmed by measurements of a larger number of offal samples.

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