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ABSTRACT

In this study, lead concentrations in various plastic toys were determined directly by solid sampling high resolution continuum source graphite furnace atomic absorption spectrometry. The toys were cut into small pieces and introduced into the graphite furnace between 0.05 and 0.7 mg without any further treatment. Lead was determined at 217.005 nm using a Pd+Mg modifier. Samples were pyrolyzed at 1000°C and atomized at 2200°C with or without gas flow at atomization stage depending on the concentration of the analyte. The lead concentration in a certified reference plastic material (ERM-EC680K) was determined in the uncertainty limits of the certified value. The limits of detection in gas-stop and gas-flow modes for 0.7 mg of sample were 0.037 and 0.93 mg kg^{-1}, respectively. The concentrations of lead in different colours plastic toys were found in the range of 0.060-9.12 mg kg^{-1}.

Keywords: Lead; Plastic; Toy; Solid sampling; Atomic absorption spectrometry

1. INTRODUCTION

Some elements such as Pb, Cd, Cr, Hg, Br, Sn and Sb are added to polymers as pigments, fillers, UV stabilizers and flame retardants. Generally these elements are added as compounds, which do not bound with polymer but create a suspension, which will may dislodge from plastic matrix in time[1]. Lead is added to plastics in order to protect it from chemical degredation and also to color them[2, 3].

Lead is one of the most critical toxic elements. Babies, infants and children, who exposed to high levels of lead, may suffer from brain and nervous system damage, behavior and learning problems, and slowed growth rate. Infants, babies and children are in close touch with toys by sucking, biting, chewing and ingesting them. Their brains and nervous systems are more sensitive to lead's damaging effects[4]. Therefore, lead in toys is restricted and strictly controlled by governments in the world. Nevertheless, from time to time, toys and other materials with high lead concentrations, which exceed the allowable limits, were recalled. For example, in December 2011, nearly 140,000 children's travel cases were recalled because the surface coating contained excessive levels of lead[5]. In 2012, about 7,000 packs of Action Figures were recalled due to excessive levels of lead in their paint [6].

Environmental Protection Agency (EPA) defined the lead concentration in painted toys as 600 mg kg^{-1} whereas U.S. Consumer Product Safety Commission (CPSC) lowered the lead concentrations in all children's products, including toys, and some kinds of furniture, to 0.009% (90 mg kg^{-1}) in paint or any similar surface coatings[7]. Academy of Pediatrics suggested that 40 mg kg^{-1} of lead which is close to the background level in soil, would be the most protective for children [8].

Determination of toxic element concentrations in different matrices is always an important subject, in point of environmental toxicity and also human health. The elemental determination in plastics, mainly metals and halogens, can be performed with many analytical procedures. Some of them require liquid samples, which needs samples to be dissolved in aqueous media i.e. atomic absorption spectrometry (AAS) [9, 10, 11] , inductively coupled plasma spectrometry (ICP-OES)[12, 13], while some of them allows multi-element determination from solid sample itself without any contact i.e. laser-induced breakdown plasma spectrometry (LIBS)[14, 15]. Determination of lead in plastics was performed by atomic absorption spectrometry (AAS) [10, 11], inductively plasma optical emission spectrometry (ICP-OES) [11-13], inductively plasma mass spectrometry (ICP-MS) [16], energy dispersion x-ray flouresence spectrometry (ED-XRF) [11, 17] and laser-induced breakdown plasma spectrometry (LIBS) [15]. The advantages and drawbacks of all those methods were extendedly reviewed by Duarte et al. [10].

The lead concentration in toys can be determined by graphite furnace atomic absorption spectrometry (GF AAS). However, in conventional GFAAS, samples are introduced to the furnace of an AAS in liquid forms after being digested prior to analysis. Introduction of solid samples directly to the graphite furnace, i.e. solid sampling GF AAS has the following advantages compared to sample digestion: (i) the sensitivity is higher since each digestion includes dilution step (ii) less (or no) time is required for sample preparation (iii) the risks of errors due to analyte loss and contamination from reagents and containers, blank readings and dilution are minimized (iv) no expensive digestion systems as well as no (or much less) toxic or corrosive reagents are required (v) analyses of very small amounts of samples (0.1 to 2 mg) are possible. On the other hand, solid sampling GFAAS (SS-GF AAS) has the following drawbacks compared to analysis of solutions: (i) the introduction of solid samples into the graphite tube is difficult and needs special equipments (ii) since very small samples are introduced to the furnace, the precision is poor due to the heterogeneity of samples and the mean of repetitive analyses of the sample may not represent the average concentration the real sample. However, this problem is still valid for digestion technique as well because the amount of sample digested (a few grams) may not represent the average concentration of the whole sample as well (iii) since the sample matrix is not decomposed as well as the amount of sample matrix introduced to the graphite furnace is high, the elimination/correction of background and interferences are more serious. However, the effective simultaneous background correction capability of high-resolution-continuum source atomic absrption spectrometers (HR-CS AAS), the use of appropriate modifiers and application of a suitable graphite furnace program, the interferences in solid sampling could be eliminated.

In this study, lead in various plastic toys with different colors was determined directly by SS-HR-CS GF AAS. The advantages of high resolution atomic absorption spectrometer were combined with those of solid sampling whereas drawbacks of the latter were eliminated after method optimization.

2. EXPERIMENTAL

2.1.Instrumentation

All measurements were carried out using a ContrAA 700 Analytik Jena (Berlin, Germany) high-resolution continuum source graphite furnace atomic absorption spectrometer (HR-CS GF AAS), equipped with a SSA600 solid sampler and a 300 W xenon short-arc lamp (XBO 301, GLE, Berlin, Germany). Argon (99.99%) was used as a purge gas. The experiments were performed by measuring Pb absorbance at 217.005 nm. Pyrolytically coated solid sampling (SS) graphite tubes (Analytik Jena, Part No. 407-A81.303) and graphite platforms (Analytik Jena, Part No. 407-152,023) were used in all measurements. The graphite furnace program used for the determination of Pb in this study is given in Table 1. Different colored various toys were purchased from markets, arbitrarily. Integrated absorbances (peak area) were used for signal evaluation.

2.2.Chemicals

All chemicals were of analytical reagent grade (Merck, Germany). Stock solution (1000 mg L^{-1}) of Pb was prepared from $Pb(NO_3)_2$ (Merck) and further diluted with ultrapure water daily (TKA Wasseraufbereitungsysteme GmbH, Niederelbert, Germany). As modifier, a mixture containing 1 mg mL^{-1} Pd and 3 mg mL^{-1} Mg in 2% HNO_3 was prepared from their nitrates (Merck, Germany).

Low-density polyethylene certified reference material (CRM) ERM-EC680K (the European Commission, Institute for Reference Materials and Measurements, Geel, Belgium), was used for method validation.

2.3.Procedure

Samples were cut into small tiny chips with a ceramic knife. A piece of sample portion below 0.7 mg was placed on the platform. The platform loaded with sample was automatically weighed and then 10 µL of Pd+Mg modifier mixture was pipetted as a modifier and directly transferred into the graphite furnace by means of solid autosampler. Lead was determined against aqueous standards. The lead concentration of every sample was given as the average of 7 portions.

3. RESULTS AND DISCUSSION

3.1. Method Development

The most important resonance lines of lead from most sensitive to least can be listed as; 217.0, 283.3, 261.4, 368.4 and 364.0 nm. Although 217.0 nm has the lowest characteristic concentration (0.08 mg L^{-1}, 1%), it does not give a beter detection limit owing to a poorer signal-to-noise ratio [18]. Moreover, 217.0 nm line has more background attenuation effect than

283.3 nm line, therefore, in most of the lead determinations by conventional AAS, 283.306 nm is used [19]. Contrary to conventional AAS, HR CS AAS with Xe arc lamp, has much higher intensity, which provides us to use 217.0 nm Pb line easily [20].

In the absence of any modifier, the maximum absorbance was obtained at an atomization temperature of 1700 °C while the maximum allowable pyrolysis temperature without any lead loss was 600 °C, which was not enough to remove the sample matrix prior to atomization step. Therefore, the background was high as well as the atomization signals were highly deterioriated and not returned to baseline even in prolonged atomization times. Similar observations were made by Duarte et al. [10] and they used a Pd+Mg modifier. In this study, a modifier was necessarily used to increase the allowable pyrolysis temperature and thereby to remove the matrix prior to atomization step as well as to obtain smooth Gaussian profiles. When Pd+Mg was added as a modifier, lead in aqueous standards and in solid plastics were remained in the furnace up to 1200 °C without any loss and the background in the spectral window between 216.877 nm and 217.122 nm, was around baseline level. Nevertheless, it was not necessary to apply 1200 °C for pyrolysis because when Pd+Mg modifier was used, smooth and narrow peaks and low background around baseline were obtained at 1000 °C as well.

In the presence of the modifier, the optimum atomization temperature was 2200 °C. Since the matrix, at least the constituents which caused interferences, was removed and the atomization temperature was higher compared to that in the absence of a modifier, the atomic absorption peaks were narrow, smooth (Gaussian) and returned to the baseline in a reasonable time (<5 s), 2200°C was applied as the optimum atomization temperature.

→Figure 1

Since the universal modifier (Pd +Mg) is satisfying for interference-free determination, the other alternative modifiers were not searched anymore. A surfactant (Triton X-100) did not cause a significant improvement on the results and thus was not used. As shown from the time and wavelength resolved (3D) absorption spectrum of a plastic sample in Fig. 1, in the presence of the modifier, no molecular and atomic absorption signal originated from the sample matrix was observed in the vicinity of the atomic absorption signal for Pb at 217.005 nm. As a result, in this study, all determinations were performed at 217.005 nm using a Pd +Mg modifier and applying the graphite furnace program given in Table 1. The most reasonable explanation for the effective use of modifier is that since plastics easily melt even at low temperatures, the modifier thoroughly mixes with the sample and intimately interacts with the analyte like a solution and protects the analyte.

Another parameter to be optimized for solid sampling analysis is the amount of sample loaded on the platform. Although the amount of analyte is in the linear range obtained with aqueous standards, the sensitivity may change depending on the sample amount. After a series of study, it was found that the linearity was generally maintained between 0.05 to 0.7 mg of sample (Fig. 2). The likely explanation for the negative deviation from linearity at sample masses above 0.7 mg is that the analyte imbedded in the high solid sample matrix is not effectively atomized. Instead, it may transported (expelled) out of furnace with rapidly vaporized sample matrix vapors or may lost again with sample vapor during pyrolsis step with matrix fumes [21, 22]. The deviation from linearity depending on the sample amount but irrespective of analyte amount always occur in all solid sampling analyses. On the other hand, at lower amounts of sample, the precision becomes poorer due to the non-uniform distribution of the analyte in the sample. Similar deteriorations were observed for other applications in the literature [23, 24].

➔ **Figure 2**

After optimization studies, the small sample chips between 0.05 and 0.7 mg were introduced to the furnace with 10 μL Pd+Mg modifier and the lead was determined applying the graphite furnace program given in Table 1. All atomization signals during analysis were followed from the monitor and if the signal did not return to the baseline, the amount of sample was reduced.

➔ **Table 1**

3.2.Figures of merit

The limit of detection (LOD) and limit of quantification (LOQ) were calculated as 3 times and 10 times the standard deviation (σ) for 10 repetitive injections of Pd+Mg modifier, i.e. 3 SD and 10 SD /slope of the calibration graph, respectively. The characteristic masses (m_0) for lead for gas-stop and gas-flow modes were 9 and 210 pg, respectively. The LODs of the method calculated for 0.7 mg of sample were 0.037 and 0.93 mg kg^{-1} in gas-stop and gas-flow modes, respectively. The LOQ values again based on 0.7 mg of sample in gas-stop and gas-flow modes were 0.12 and 0.31 mg kg^{-1}, respectively. The m_0, LOD ve LOQ values were at the same level as those found by Duarte et al [10]. LOD and LOQ are below the maximum limit allowed by CPSC (60 mg kg^{-1}). Figures of merit for lead determination are given in Table 2.

In order to test the accuracy of the method, the lead concentration of a plastic CRM (ERM-EC 680K) was determined. Using linear calibration against aqueous standards, the lead concentration in the CRM was found between the uncertainty limits of the certified value at 95% confidence level. For some samples, which have lower Pb content than the LOD with gas flow during atomization stage gas flow was stopped during atomization. By this way, the sensitivity of the method was increased and the LOD was lowered below the lead concentrations of many samples. The same tube and platform was used during the whole analysis which corresponds at at least 300 firings. Since sample digestion was eliminated, in spite of more repetitions compared to digestion, the whole analysis was completed much faster compared to digestion technique.

➔ **Table 2**

3.3. Determination and distribuition of lead in plastics

Generally, the RSD values for solid sampling are higher than those obtained for repetitive introductions of the solutions due to non-homogeneous of distribution the analyte in sample. Very small amounts of sample portions introduced to the furnace for solid sampling analysis (<0.7 mg) are insufficent to represent the average analyte concentration in the sample. The smaller the sample portions to be analyzed, the lower the precision is. As shown from Fig.3, the analyte concentrations in different portions of the same sample were scattered in a wide range which can be attributed to random errors during measurement procedure as well as heterogeneity of the analyte distribution in the sample.

The mean concentration and RSD change with the number of sample portions analyzed depending on the heterogenity of the analyte distribution in samples [24, 25]. In fact, even the certificated values in CRMs are generally guaranteed only if at least 50 to 100 mg of sample portion is used (or digested) for analysis. Therefore, the number of solid sample portions to be analyzed should be enough to represent the average analyte concentration in the sample satisfactorily. In solution technique, the lower number of repetition compared to solid sampling seems to be a time-saving advantage. However, this advantage is overcompensated by time-consuming digestion procedure. In addition, the analyte loss and contamination by reagents and containers are other risks of digestion procedure for accuracy.

The use of very small amounts in solid sampling could be benefited to estimate the homogeneity of analyte distribution. In order to determine the distribution of lead in plastics, the homogeneity factor (H_E) was calculated from

$H_E = RSD \times (m)^{0.5}$ (1)

where m is the average sample mass as milligram, RSD is the relative standard deviation of the analyte concentrations due to analyte heterogeneity in the sample. It is assumed that if the H_E value is lower than 10, then the analyte distribution is accepted to be homogeneous [25-28].

In solid sampling analysis, the relative standard deviation of the results (RSD_{total}) is originated from the random errors of instrumental uncertainities ($RSD_{instrumental}$) and the heterogeneity of the analyte distribution in the sample ($RSD_{heterogeneity}$). RSD_{total} can be expressed as

$RSD^2_{total} = RSD^2_{instrumental} + RSD^2_{heterogeneity.}$ (2)

RSD_{total} is determined from analysis of different solid sample portions whereras $RSD_{instrumental}$ is found from the relative standard deviation of repetitively pipetted a calibration standard with Pd+Mg modifier which do not contribute to analyte heterogeneity in the sample. Assuming that $RSD_{instrumental}$ is almost constant, $RSD_{heterogeneity}$ and then H_E values are calculated from Eqns 2 and 1, respectively. When the lead was determined in 7 or more portions of a sample, the mean concentrations and the H_E values for different set of experiments were generally reached to almost constant values. Therefore, the lead concentration of every sample was given as the average of 7 portions.

➔ **Figure 3**

Finally, the lead concentrations and H_E values in various PVC toys were determined and the results were given in Table 3. Generally, the H_E values were below 10 which show a homogeneous analyte distribution. The precision and homogeneity are better than expected for a solid sampling. Although some of the samples were bought from bazaars (nonbranded and there was no information about the source), the lead concentrations were much below the allowable limits reported by CPSC and EPA.

➔ **Table 3**

4. CONCLUSION

It was proved that SS-HR-CS GFAAS could be appropriately used for the determination of lead in plastic toys with almost no sample preparation and using aqueous standards for calibration. All the advantages of solid sampling were benefited and its drawbacks were eliminated after method optimization. Samples were introduced directly to the furnace as well as no hazardous and corrosive chemicals were used. The only chemical used was the modifier. The method is fast, simple and environment friendly. LOD value was low enough to determine the lead below the maximum allowable limit reported by CPSC (60 mg kg^{-1}). By taking the advantages of very small amounts required, the homogeneity of lead distribution in the samples could be determined. It was found that the lead in plastic toys was quite homogeneously distributed.

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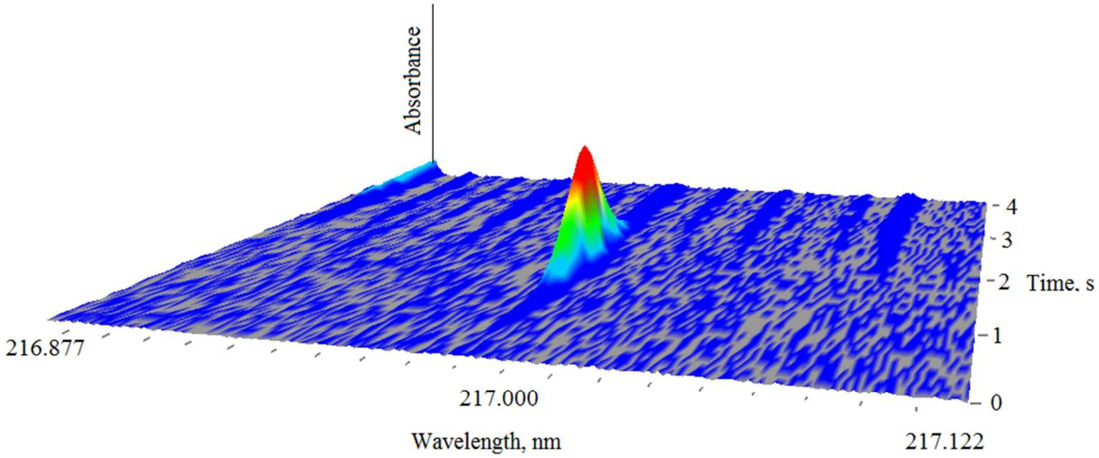

Figure 1: Time and wavelength resolved (3D) absorption spectrum of a plastic sample in the vicinity of 217.005 nm obtained according to graphite furnace program given in Table 1 and in the presence of Pd +Mg modifier.

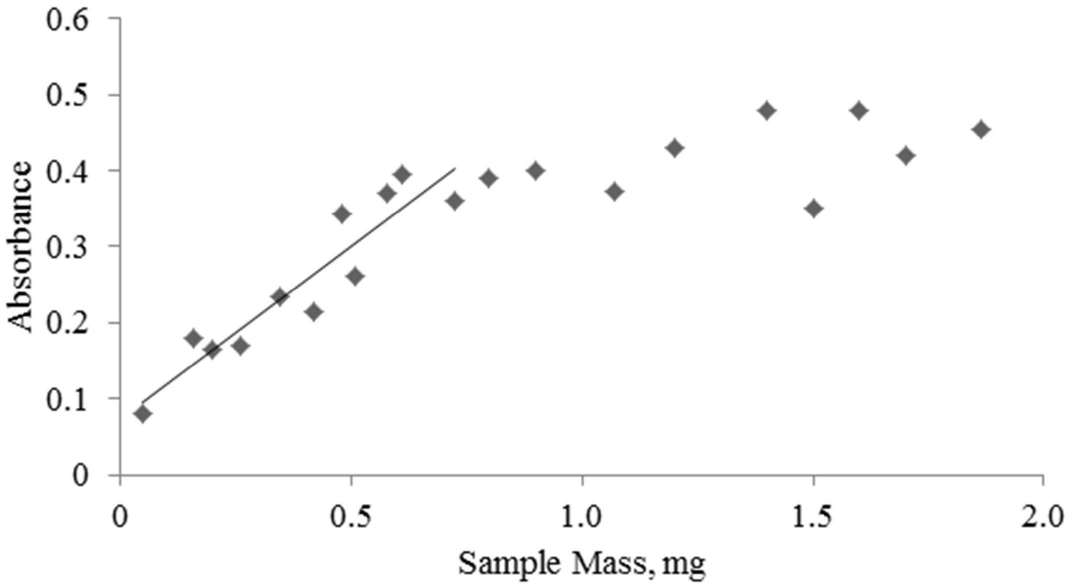

Figure 2: The effect of sample mass on the sensitivity of lead.

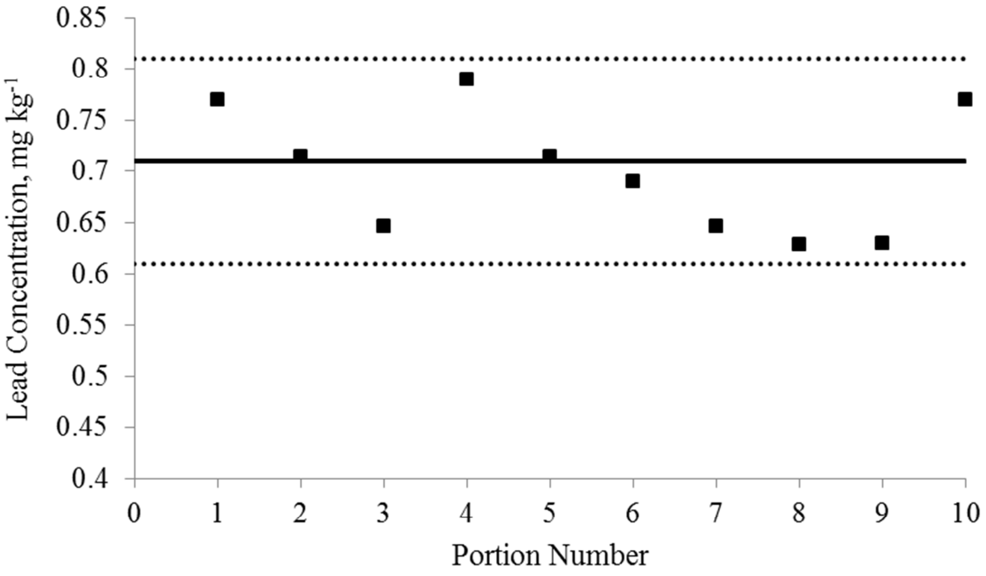

Figure 3. Distribution of lead concentrations in different sample portions of a PVC toy sample. (solid horizontal line is the mean concentration; dotted lines are 3SD values of measurements)

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Table 1: Optimized graphite furnace program for lead determination in plastics by HR-CS GF AAS

		Temperature, °C	Ramp, °C s^{-1}	Hold, s	Gas Flow, mL min^{-1}
1	Drying	110	5	30	2.0
2	Pyrolysis	1000	300	10	2.0
3	Gas Adaption	1000	0	5	2.0[a]
4	Atomize	2200	1500	4	2.0[a]
5	Clean	2450	500	4	2.0

[a] Gas-Stop was applied for samples with low Pb concentrations.

Table 2: Figures of merit for lead determination in plastics by HR-CS GF AAS.

Parameter value	Without gas flow	With gas flow [a]
Characteristic Mass, m_0, pg	9	210
Limit of Detection, LOD, mg kg^{-1} [b]	0.037	0.93
Limit of Quantification,LOQ, mg kg^{-1} [b]	0.12	3.10
Sample mass range introduced, mg	0.05-0.7	0.05-0.7
Regression Coefficient	0.999	0.998

[a] 2.0 L min^{-1}

[b] Calculated for 0.7 mg of sample.

Table 3: Concentrations with confidence intervals at 95 % confidence level and homogeneity factors of lead in CRM and various plastic toys (N:7)

	Concentration (mg kg^{-1})[a]	H_E
CRM (ERM-EC 680K)	13.8±1.2[b]	3.2
Sample -1 (Black) [c]	0.060±0.008	4.8
Sample -2 (Black) [c]	0.064±0.010	6.3
Sample -3 (Black) [c]	0.072±0.008	7.2
Sample -4 (White) [c]	0.718±0.092	5.4
Sample -5 (White) [c]	0.716±0.106	6.2
Sample -6 (White) [c]	0.733±0.105	7.3
Sample -7 (Yellow) [c]	0.131±0.017	6.2
Sample -8 (Yellow) [c]	0.072±0.009	5.4
Sample -9 (Yellow) [c]	0.089±0.011	5.2
Sample-10 (Red)	8.263±1.275	7.2
Sample -11 (Red) [c]	0.057±0.007	5.6
Sample -12 (Red)	8.316±1.205	6.7
Sample -13 (Red)	9.118±1.415	7.2
Sample -14 (Green) [c]	0.300±0.030	4.4
Sample -15 (Green)	1.346±0.168	5.4
Sample -16 (Green) [c]	0.542±0.062	4.2
Sample -17 (Blue) [c]	0.226±0.028	5.4
Sample -18 (Blue) [c]	0.243±0.035	6.4
Sample -19 (Blue) [c]	0.264±0.040	6.6
Sample-20 (Pink)	1.773±0.225	7.2
Sample-21 (Pink)	1.432±0.220	8.4

Sample-22 (Pink)	1.234±0.215	9.5
Sample-23 (Orange) [c]	0.480±0.080	8.3
Sample-24 (Orange) [c]	0.432±0.075	9.4
Sample-25 (Orange) [c]	0.467±0.073	7.2

[a] mean ± $ts/N^{1/2}$ at 95% confidence level

[b] Certified value is 13.6±0.5 mg kg^{-1}

[c] Gas-Stop was applied for samples with low lead concentrations

Graphical Abstract