Online preconcentration for the determination of lead, cadmium and copper by slotted tube atom trap (STAT)-flame atomic absorption spectrometry

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Abstract
An online sensitivity enhancement by using atom trapping in flame atomic absorption spectrophotometry was examined for increasing the residence time of the analyte atoms in the light path. For this purpose, various parameters of quartz tubes of the slotted tube atom trap were tested. The studied parameters include the internal diameter, the length of the upper slot and the wall thickness of quartz tube. The best sensitivities as high as 7-fold, 13-fold and 3-fold enhancement were achieved by the tubes having an internal diameter of 6 mm, an upper slot length of 1.0 cm and the wall thickness of 1.5 mm for lead, cadmium and copper, respectively. The limits of quantitation were found to be 30 ng mL$^{-1}$ for Pb and 3 ng mL$^{-1}$ for Cd and 30 ng mL$^{-1}$ for Cu by the optimized method. The achieved technique was applied to determine the concentrations of Pb, Cd and Cu in different plant leaves taken around cement and textile industries.

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Keywords: The sensitivity improvement; Flame atomic absorption spectrometry; Lead; Cadmium; Copper; Plant leaves

1. Introduction
Humans are exposed to Cd, Pb and Cu by food intake and inhaling air which is polluted by environmental conditions and industrial emissions. The accumulation of these metals in human body can have middle and long-term health risks and can adversely affect the physiological functions.

For a long time, it is known that lead is toxic for brain, kidney and reproductive system and can also cause impairment in intellectual functioning, infertility, miscarriage and hypertension. Several studies have shown that lead exposures in school-aged children can significantly reduce IQ and has been associated with aggressive behavior, delinquency and attention disorders. Due to its malleability, low melting point, and ability to form compounds, Pb has been used in hundreds of products such as pipes, solder, brass fixtures, crystal, paint, cable, ceramics, and batteries [1]. As a result, populations in, at least, 100 countries are still exposed to air pollution with lead in spite of banning the usage of lead in gasoline.

Cd competes with Zn for binding sites and can therefore interfere with some of Zinc’s essential functions. Thus, it may inhibit enzyme reactions and utilization of nutrients. Cd can generate free radical tissue damage because it may be a catalyst to oxidation reactions. Furthermore, excessive Cd exposure can cause renal damage, reproduction problems, cardiovascular diseases and hypertension. There are several sources of human exposure to Cd, including employment in primary metal industries, production of certain batteries, some electroplating processes and consumption of tobacco products [2]. Consequently, it was reported by International Agency Research on Cancer (IARC) that through inhalation cadmium could cause lung cancer in humans and animals [3].

Copper is a necessary element as a component of more than 30 enzymes including superoxide dismutase (SOD), caeruloplasmin, cytochrome oxidase, ascorbate oxidase and tyrosinase in the human body. On the other hand, Cu has adverse effects on human health at its high concentrations. Furthermore, in vitro studies have shown that cancer cells in a high copper environment find it easy to proliferate into tumor. It was reported that copper is a well known pro-oxidant and may participate in metal-catalyzed peroxidation of lipids as similar to iron [4].

Recently, increased attention is paid to the use of plant parts such as leaves, shoots and barks as biomonitors. In the most...
used expression, biomonitoring may be defined as the use of bioorganisms or biomaterials to obtain information on certain compounds in biosphere. The advantages of using of biomonitoring for environmental surveillance lie in the lower cost as compared to direct methods of pollution measurement, since no collecting or measuring equipment has to be installed and protected against vandalism. If the biomonitoring is widely distributed and occur frequently enough they can be used over large areas for recording and evaluating heavy-metal inputs. Furthermore, they make it possible to identify sources of emissions and verify the overland transportation of individual elements. As a result, many plant species are useful for biomonitoring atmospheric deposition of pollutants [5].

The World Health Organization (WHO) [6] established provisional tolerable weekly intakes (PTWIs) of Cd and Pb of 0.007 and 0.025 mg kg$^{-1}$ body weight, respectively, for all human groups. Therefore, analytical techniques with high sensitivity are required for detection of these metals. These techniques include electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), anodic stripping voltammetry (ASV), differential-pulse polarography (DPP), and inductively coupled plasma-mass spectrometry (ICP-MS).

It is well known that the flameless atomic absorption spectrometry is a more sensitive technique than flame atomic absorption spectrometry (FAAS). However, relative to the later technique, flameless AAS has some disadvantages such as its high cost, slowness and greater proneness to interferences [7]. Although, effective chemical modifiers, background correction systems, improved furnace and platform designs and careful optimization of temperature programs were used to remove the interferences [8], it is still widely studied in relation to the interferences in this field of flameless AAS [9]. If both of these methods can be used, FAAS should be preferred to flameless AAS because FAAS is faster, cheaper and does not require expert operators.

Therefore, there are continuing efforts to enhance the sensitivity of FAAS despite its being the mature analytical (many believe “over the hill”) technique. These efforts can be classified as offline and online methods. The offline methods include the most of preconcentration methods such as liquid–liquid extraction, adsorption, precipitation, solid phase extraction [10–13] except their several special applications. The sensitivity of FAAS is limited by several factors. The analyte atoms generated in the flame pass rapidly and continuously through the measurement zone during sample aspiration. A further limitation is the poor efficiency of the nebulizer/burner system. A maximum of 10% of the aspirated sample solution reaches the flame. The sensitivity can be improved if the atomic vapor has been constrained to remain in the light path for a long time. In a review article, Matusiewicz recently discussed in detail the techniques examined for this purpose [14]. Among these methods, atom-trapping technique is designed in two different shapes: the slotted quartz tube and the water-cooled silica tube. Although these techniques that can be called as online methods were firstly described 25 years ago [15], it is evident that the scientific literature on this topic has increased recently [14]. The water-cooled silica system, in addition to having the advantage of being more sensitive to improvement than the slotted quartz tube, has the disadvantage of needing a very large volume of a sample due to the longer aspiration times as long as 2 min for one measurement [16–18]. In another application of atom trapping technique, the re-volatilization of analytes using organic solvent in a more concentrated form into the atomizer system was studied [19]. However, this technique has also the disadvantages mentioned above for the water-cooled silica system as well as the possible imprecise measurements.

Keeping atoms in the optical path with the so-called slotted-tube atom trap (STAT) system, as illustrated in Fig. 1, has been found to be more popular recently [14,21]. Because quartz has a sufficiently high melting point and a low thermal expansion coefficient, it has been chosen as the material for the atom trap. The sensitivity improvement is attributed to the increased residence time of the analyte atoms in the light path due to slower flame speed in STAT. Furthermore, the more stable chemical environment due to homogenous temperature in quartz tube enhances the numbers of neutral atoms, thereby increasing the sensitivity. In the STAT system, a double-slotted quartz tube with the length of the upper slot shorter than that of the lower slot is installed above the burner and placed into the flame gases and analyte atoms using pneumatic nebulizer system (Fig. 1). The optimization of the slotted tube using various designs and parameters, such as exit holes, tube length and tube materials, was reviewed in detail [14]. In that review [14], it was also reported that the achieved improvements in the sensitivity were in the range of 2- to 5-fold. In recent times, 10-, 6- and 3-fold improvements in the sensitivities of Cd, Pb and Cu were achieved by using the tube having the diameter of 6.0 mm, the upper slot length of 2.3 cm, the tube length of 12 cm and the lower slot length of 5 cm, respectively [20,21].

In other studies [22–26], cadmium, lead and Cu concentrations in the biological and environmental samples, such as human urine, fruits, milk, soil and water, were determined by using direct FAAS-STAT and/or together with preconcentration methods. In those studies, 2.5- and 5-fold improvements in the sensitivity of FAAS were achieved for lead and cadmium using the STAT having a diameter of 8 mm and an upper slot of 4 cm, respectively.

In this study, the length of the upper slot, the internal diameter and the wall thickness of quartz tube in STAT were systematically changed in order to improve the sensitivity of FAAS. The obtained best conditions were applied to the determinations of Cd, Pb and Cu concentrations in the plant leaves taken around
industrial areas such as cement factory and textile industry to examine their biomonitoring possibilities.

2. Experimental

2.1. Apparatus and reagents

An ATI UNICAM 929 Model flame atomic absorption spectrophotometer (FAAS) equipped with ATI UNICAM hollow cathode lamps (HCL) was used for the metal determinations. The acetylene–air flame in FAAS in which the optimal conditions were studied is provided in the manufacturer’s instructions for the spectrophotometer. A domestic microwave oven (Kennywood) was used for the digestion of the tissues. The STAT was used to improve the sensitivity of FAAS.

Unless stated otherwise, all chemicals used were of analytical-reagent grade. During all analytical work, double-distilled water was used. All glass apparatus were kept permanently full of 1 mol L$^{-1}$ distilled water when not in use. In the digestion procedures, concentrated nitric acid (65%, Merck) and hydrogen peroxide (35%, Merck) were used. Stock solutions of the metals (1000 mg L$^{-1}$) were prepared by dissolving their nitrate salts in 1.0 mol L$^{-1}$ nitric acid.

To assess the reliability of measurements, some samples were analyzed by PerkinElmer Elan 9000 inductively coupled plasma-mass spectrometry (ICP-MS) at ACME Analytical Labs in Canada.

2.2. Changes made on the STAT

Various changes on quartz tubes were studied to enhance the sensitivity. These changes included the internal diameter, the length of the upper slot, the wall thickness of quartz tube and the length of tube. Among the other suspected factors, lower slot length depends on the slot of the burner. Hence, it is obvious that the change in its length has not improved the sensitivity. The height of the tube over the burner was always adjusted to obtain a maximum absorbance. The studied quartz tube can be used only in the flame of the acetylene–air mixture. The changes made on the quartz tubes are given in Table 2. In all designs, the length of the lower slot was 50 mm.

2.3. Sampling and sample preparation

The studied plant leaves including Ficus carica, cherry, apple, Punica granatum, Prunus domestica, maize, Morus L., cedrus and pieca were obtained around Gaziantep city and transferred to laboratory in plastic bag. The samples were washed with tap water and then rinsed with distilled water. After drying at 70°C, 0.5 g of samples were transferred into flask (Pyrex) and digested by using dry ot/and microwave (MW) ashing methods.

2.4. Dry ashing

The dried samples were heated gradually in a furnace at 200°C for 15 min, at 300°C for 10 min, at 400°C for 10 min, and ashed at 480°C for 4 h.

The mixture of concentrated nitric acid/hydrogen peroxide (1/1) (3 mL for 1 g of dried samples) were added to the ashed sample and heated up to drying. This procedure was repeated. After cooling, 3 mL of 1 mol L$^{-1}$ nitric acid was added and centrifuged, if necessary. The clear solutions were measured by FAAS and STAT-FAAS for metal determinations. The blank digests were carried out in the same way.

2.5. Microwave (MW) ashing

To assess the losses of the studied metals in dry digestion procedure, some samples were also digested by using MW energy. Approximately 0.2 g of dried samples was transferred into Teflon bomb and 1 mL of the mixture of HNO$_3$/H$_2$O$_2$ was added. The bomb was closed, placed inside the microwave oven, and microwave radiation was carried out for 3 min at 450 W. After a 4-min cooling period and adding 1 mL of the same acid mixture, the microwave radiation was repeated for 3 min. After cooling, the digest was diluted to 3 mL by adding 0.1 mol L$^{-1}$ HNO$_3$. The solution was centrifuged, if necessary. The clear solution was measured by FAAS and STAT-FAAS for metal determinations. Blank digests were carried out using the same procedures.

3. Results and discussion

It is known that the enhancement in the sensitivity of FAAS is importantly dependent on the flow rate of the aspirated solution. In this study, the speed of the aspirated solution was measured as 1 mL/11 s. Table 1 shows the obtained results for various designs of quartz tube together with the applied changes. The effect of parameters, such as, the internal diameter and the wall thickness of the tube, length of the upper slot and length of the tube on the improvement of sensitivity were examined. The observed improvements in the sensitivity can be summarized as follows.

Figs. 2–5 were obtained from the data given for Pb and Cd in Table 1. As it can be seen from these Figures, the sensitivity enhancement depending on the lengths of the upper slot is found significantly higher than that on the other parameters. Moreover, more improvements in the sensitivities are obtained using the tube having length of 12 cm as compared with the length of 11 cm. The sensitivity enhancement depending on tube length is higher in Cd than in Pb. Finally, higher enhancement in the
Table 1
The obtained improvements in the sensitivity of Pb, Cd and Cu by using STAT-FAAS

<table>
<thead>
<tr>
<th>Diameter of tube (mm)</th>
<th>Length of upper slot (cm)</th>
<th>Length of tube (cm)</th>
<th>Enhancement in sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pb</td>
<td>Cd</td>
</tr>
<tr>
<td>6(^a)</td>
<td>4</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>6(^a)</td>
<td>3</td>
<td>12</td>
<td>5.5</td>
</tr>
<tr>
<td>6(^b)</td>
<td>2.5</td>
<td>12</td>
<td>5.5</td>
</tr>
<tr>
<td>6(^b)</td>
<td>2</td>
<td>12</td>
<td>6.5</td>
</tr>
<tr>
<td>6(^b)</td>
<td>1.5</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td>6(^b)</td>
<td>1</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td>6(^b)</td>
<td>0.5</td>
<td>12</td>
<td>7</td>
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<tr>
<td>5(^a)</td>
<td>3</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>5(^a)</td>
<td>2</td>
<td>12</td>
<td>5</td>
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<tr>
<td>5(^a)</td>
<td>1</td>
<td>12</td>
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<td>5(^a)</td>
<td>0.5</td>
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<td>6(^a)</td>
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<td>5</td>
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<td>11</td>
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<td>6(^a)</td>
<td>2</td>
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<td>6(^a)</td>
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<td>6(^a)</td>
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</tr>
<tr>
<td>6(^a)</td>
<td>0.6</td>
<td>11</td>
<td>5.5</td>
</tr>
</tbody>
</table>

L of Q as ng mL\(^{-1}\) with direct FAAS 200 40 80

The lengths of the lower slot are 5 cm.

\(^a\) Tube thickness is 1.5 mm.

\(^b\) Tube thickness is 1.0 mm.

Fig. 3. The sensitivity enhancements for Pb depending on the changes in length of upper slot and thickness of 1.5 mm, using tube length of 11 cm.

Fig. 4. The sensitivity enhancements for Cd depending on the changes in length of upper slot, using tube length of 12 cm and thickness of 1.5 mm.

As it can be seen from the data for Cu in Table 1, the sensitivity enhancement depending on the lengths of the upper slot is found higher. Moreover, higher enhancement in the Cu sensitivity of lead and cadmium are observed using the tube thickness of 1.5 mm, as compared with the tube of 1.0 mm. This can be attributed to the more numbers of neutral atoms in the more stable chemical environment due to the homogenous temperature, in the tube thickness of 1.5 mm. As it can be seen from Table 1, the sensitivity is not improved much when the tube has the diameter of less than 6 mm for both of Pb and Cd. This result can be related to the diameter of light, which is larger than 5 mm, particularly in entrance of the tube. As a result, the determination of Pb and Cd concentrations as low as 30 and 3 ng mL\(^{-1}\) were achieved by the modified STAT-FAAS method in which the tube had the length of 1.0 cm and the diameter of 6 mm in the upper slot.

The obtained calibration graphs for Pb by using different designed tubes were given in Fig. 6, and the calibration curves were found to be linear in the given ranges. The equations of the calibration curves for Pb without STAT and with most sensitive STAT are as follows:

\[ Y = 0.0468X + 0.5342 \quad R^2 = 0.9995 \] for Pb without STAT (200–2000 ng mL\(^{-1}\)).

\[ Y = 0.3056X – 0.0734 \quad R^2 = 0.9999 \] for Pb with most sensitive STAT (30–400 ng mL\(^{-1}\)).

\[ Y = 0.3042X + 38.93 \quad R^2 = 0.9997 \] for Pb using standard additions (0.0–400 ng mL\(^{-1}\)), respectively.

The obtained calibration graphs for Cd by using different designed tubes were given in Fig. 7, and the calibration curves were found to be linear in the given ranges. The equations of the calibration curves for Cd without STAT and with most sensitive STAT are as follows:

\[ Y = 0.2437X + 0.5342 \quad R^2 = 1.0000 \] for Cd without STAT (40–800 ng mL\(^{-1}\)).

\[ Y = 3.1284X + 0.3547 \quad R^2 = 0.9999 \] for Cd with most sensitive STAT (3.0–40 ng mL\(^{-1}\)).

\[ Y = 3.1074X + 31.288 \quad R^2 = 0.9996 \] for Cd using standard additions (0.0–40 ng mL\(^{-1}\)), respectively.
sensitivity is observed using the tube thickness of 1.5 mm, in comparison to the tube of 1.0 mm, similar to Pb and Cd. The sensitivity is decreased much when the tube has the diameter of less than 6 mm for Cu unlike Pb and Cd. This result can be attributed to the diameter of light of copper HCL lamp, which is larger than 5 mm, particularly at the entrance of the tube.

The calibration graphs together with standard additions graph for Cu by using the designed tubes including the length of upper slot of 1.0 cm, the length of tube of 11.0 cm were examined, and the calibration curves were found to be linear in the given ranges. The equations of these curves for Cu are as follows:

\[
Y = 0.102X - 0.2R^2 = 0.9999 \text{ for Cu without STAT (100–1000 ng mL}^{-1}).
\]

\[
Y = 0.318X - 0.3902R^2 = 0.9999 \text{ for Cu with most sensitive STAT (30–400 ng mL}^{-1}), \text{ by using tube thickness of 1.5 mm.}
\]

\[
Y = 0.2234X - 0.3171R^2 = 0.9999 \text{ for Cu with STAT (30–400 ng mL}^{-1}), \text{ by using tube thickness of 1.0 mm.}
\]

\[
Y = 0.3173X + 41.646R^2 = 0.9997 \text{ for Cu using standard additions (0.0–400 ng mL}^{-1}).
\]

As a result, the determinations of Cu concentrations as low as 30 \(\mu\)g L\(^{-1}\) were achieved by the modified STAT-FAAS method in which the tube had the length of 1.0 cm, the diameter of 6 mm in the upper slot and the wall thickness of 1.5 mm.

The main advantages of the STAT-FAAS compared to the conventional FAAS lie in the increased sensitivity and in the reduction of potential interferences because the former technique allows greater dilution of the sample. Devitrification of the slotted quartz tube was prevented by aspirating of a 1\% (m/v) lanthanum solution. As a result, the service life of quartz tube was increased. On the other hand, it was observed that the service life of the quartz tube was related to the wall thickness of the tubes. The measurements more than 100 cycles can be done using the tube having a wall thickness of 1.5 mm.

3.1. Analytical performance

Levels of Pb, Cd and Cu in the reagent blanks in the total analytical steps were found to be 8.0, 0.5 and 3.5 ng mL\(^{-1}\) with standard deviations (s) of 1.0, 0.1 and 0.7 ng mL\(^{-1}\), respectively. Therefore, the detection limit, defined as three times of the \(s\) values of blanks, was calculated as 3.0, 0.3 and 2.1 ng mL\(^{-1}\). Limit
of quantitation for Pb, Cd and Cu were found as 200, 40 and 80 ng mL\(^{-1}\) for direct FAAS and 30, 3 and 30 ng mL\(^{-1}\) for the best conditions of sensitivity. For total analytical procedure containing the digestion procedure, the relative standard deviations measured for concentrations of 100, 20 and 80 ng mL\(^{-1}\) of Pb, Cd and Cu were found as 5, 3 and 4%, respectively (\(n = 8\)).

The accuracy of the method was studied by examining the Standard Reference Material-Tomato Leaves-1573a. The results were given in Table 2. It can be seen that the recovery values for Cd and Cu in Tomato Leaves-1573a was found as 96 and 98%, respectively.

In addition, the plant leaves containing the highest concentrations of Pb and/or Cd and/or Cu were analyzed by using both direct conventional FAAS and the STAT-FAAS. The obtained results using STAT-FAAS were compared with those obtained from the direct conventional FAAS. It was observed that the results obtained from STAT-FAAS were agreed with the results obtained from the conventional FAAS, at least 95%. In addition, the recoveries of Pb, Cd and Cu from the plant leaves fortified with the Pb, Cd and Cu were used to test of the accuracy of the modified method. The concentrations of Pb, Cd and Cu spiked to the samples are in the range of 100–300, 10–30 and 40–60 ng mL\(^{-1}\), respectively. It was found that at least 96% of Pb, Cd and Cu added to the plant leaves were recovered. The effect of contamination was eliminated by subtracting the obtained values for blanks. In addition, to overcome the enhancement or suppression due to the presence of major components of the leaves matrix, calibration solutions were performed within the sample matrix itself. On the other hand, the standard additions method for the determination of Pb, Cd and Cu in the plant samples was examined. As described above, the slopes of the calibration curves were compared with the slopes obtained by the standard additions method. These results indicate the absence of chemical interferences, because the slopes of calibration curves and standard additions are identical for three studied elements. Therefore, the calibration graphs were used to determine Pb, Cd and Cu in the studied plant samples. The optimized method was applied to the determination of lead, cadmium and copper in different plant leaves using the quartz tube having the best conditions described above.

Finally, it is observed that there is not a significant difference between the data (Table 2) obtained by FAAS and ICP-MS methods using t-test at confidence level of 90% for the studied metals. Similarly, Pb, Cd and Cu concentrations in plant samples were found to be in acceptable limits by using dry ashing in considering t-test at confidence level of 90% as compared with the MW ashing results. No losses of Pb and Cd in dry ashing can be attributed to the differences in matrices [11].

### Table 2

<table>
<thead>
<tr>
<th>Plant</th>
<th>Pb (mg kg(^{-1}))</th>
<th>Cd ((\mu g ) kg(^{-1}))</th>
<th>Cu (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement (ICP-MS)</td>
<td>Textile (ICP-MS)</td>
<td>Cement (ICP-MS)</td>
</tr>
<tr>
<td>C. libani</td>
<td>7.6 ± 0.9</td>
<td>1.3 ± 0.3 (1.3 ± 0.2)</td>
<td>39 ± 8</td>
</tr>
<tr>
<td>P. E. L.</td>
<td>2.1 ± 0.5 (1.8 ± 0.3)</td>
<td>2.1 ± 0.3 (2.3 ± 0.3)</td>
<td>66 ± 12 (61 ± 5)</td>
</tr>
<tr>
<td>A. C. L.</td>
<td>11 ± 2 (10 ± 1)</td>
<td>11 ± 4</td>
<td>18 ± 2 (19 ± 5)</td>
</tr>
<tr>
<td>Eriobotrya Japonica</td>
<td>0.9 ± 0.5 (3.4 ± 0.5)</td>
<td>1.5 ± 0.4 (1.8 ± 0.1)</td>
<td>176 ± 26 (200 ± 32)</td>
</tr>
<tr>
<td>R. conica</td>
<td>4.0 ± 0.5 (2.7 ± 0.4)</td>
<td>50 ± 5 (46 ± 6)</td>
<td>3.2 ± 0.4 (3.6 ± 0.2)</td>
</tr>
<tr>
<td>P. domestica</td>
<td>6.7 ± 1.2</td>
<td>7 ± 2</td>
<td>4.0 ± 0.8</td>
</tr>
<tr>
<td>P. Granatum</td>
<td>6.8 ± 0.8</td>
<td>3.5 ± 0.6</td>
<td>4.7 ± 0.6</td>
</tr>
<tr>
<td>C. oblonga</td>
<td>4.4 ± 0.3 (4.4 ± 0.4)</td>
<td>112 ± 13 (103 ± 10)</td>
<td>5.3 ± 0.5 (5.9 ± 0.8)</td>
</tr>
<tr>
<td>F. carica</td>
<td>3.0 ± 0.2</td>
<td>25 ± 5</td>
<td>2.5 ± 0.3</td>
</tr>
<tr>
<td>J. magna</td>
<td>5.0 ± 0.4</td>
<td>18 ± 4</td>
<td>25 ± 7 (28 ± 6)</td>
</tr>
<tr>
<td>A. P. L.</td>
<td>2.6 ± 0.4 (2.9 ± 0.3)</td>
<td>30 ± 5</td>
<td>32 ± 4</td>
</tr>
<tr>
<td>A. P. L.</td>
<td>2.4 ± 0.4 (2.3 ± 0.3)</td>
<td>50 ± 5</td>
<td>2.8 ± 0.5</td>
</tr>
<tr>
<td>P. domestica</td>
<td>10 ± 2 (9 ± 4)</td>
<td>50 ± 5</td>
<td>2.8 ± 0.5</td>
</tr>
<tr>
<td>SRM-Tomato leaves-1573a</td>
<td>–</td>
<td>Certified 1520 ± 40</td>
<td>Certified 4.70 ± 0.14</td>
</tr>
</tbody>
</table>

The values in parenthesis are obtained by using ICP-MS. These values are obtained by using MW ashing.

3.2. Application

Lead, Cd and Cu concentrations in the leaves of various plants are summarized in Table 2. As it can be seen that lead concentration (dw) ranges from 0.8 to 11 µg g\(^{-1}\) for the cement factory area and 1.1–3.5 µg g\(^{-1}\) for the textile industry area. This variation may be depending on varying uncontaminated and polluted areas by cement factory. The authors generally determined the metal concentrations in plants to evaluate atmospheric pollution [5,27,28]. From Table 2, Pb concentrations in the leaves of C. libani taken around cement factory were found to be higher about five times than in the textile area.

Cd concentrations in leaves of E. Japonica and C. oblonga plants were found to be 10-fold higher than in those other plants taken around cement factory. As a result, the leaves of these two plants can be used as biomonitors for environmental Cd pollution. Higher Cd concentration (367 ng g\(^{-1}\)) in E. Japonica leaves taken around textile industry than in those other plants taken from the same area, and in the same plant taken around cement factory also support this conclusion. The observed Cu concentrations in the studied plant leaves are in acceptable limits.

4. Conclusions

It has been demonstrated that the optimized technique can be used for the determination of ultratrace concentrations of...
Pb, Cd and Cu in analytical samples. The proposed method has some advantages such as high speed, less risk of contamination, low cost and easy manufacturing of the required quartz tube. Although the achieved improvement is modest (7-fold for Pb, 13-fold for Cd and 3-fold for Cu), the modified online method has much importance in comparison with the other offline enrichment techniques such as adsorption or extraction because of its simplicity and instantly applicability.

Finally, the sensitivity between the FAAS and flameless AAS for some elements such as lead and cadmium is bridged gradually via the atom trap in FAAS. In this study, the sensitivity improvement, which has not been obtained so far by STAT, has been achieved for Pb and Cd by using very simple modifications in the STAT. The limits of quantitation were found to be 30 ng mL\(^{-1}\) for Pb, 3 ng mL\(^{-1}\) for Cd and 30 ng mL\(^{-1}\) for Cu. The required volume of sample for this method is less in comparison with other enrichment methods; i.e., only 0.9 mL of solution is sufficient for three metal determinations.

References