Chem. Anal. (Warsaw), **45**, 325 (2000) **REVIEW**

Sample Preparation Procedures for Total Mercury Determination in Materials of Natural Origin

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Key words: mercury determination, chemical sample pretreatment, cold vapor atomic absorption spectrometry, review

The interest in mercury determination in materials of natural origin is closely connected with the toxicity of this element as well as its organic and inorganic compounds. The main difficulties in the analysis of diverse samples result from high volatility of mercury itself and its compounds; however some of them are very stable. Hence the stage at which the analyte is being quantitatively transferred to a solution in an appropriate form without loss is very important. There are many papers devoted to the research into this problem. This paper presents the methods recommended by various authors and the main problems of chemical pretreatment of natural materials for the purpose of mercury determination are discussed. An account of the influence of different components of an analytical sample solution on the results of mercury determination by cold vapor atomic absorption spectrometry is given.

Zainteresowanie metodami oznaczania rtęci w materiałach naturalnych związane jest z silnie toksycznymi właściwościami tego pierwiastka, jak również jego związków organicznych i nieorganicznych. Szczególne trudności, w procesie analizy różnego rodzaju próbek, spowodowane są dużą lotnością samej rtęci oraz jej związków, przy czym niektóre z nich odznaczają się znaczną trwałością. Stąd istotny jest etap ilościowego przeprowadzania analitu do roztworu w odpowiedniej formie i przy pełnym zabezpieczeniu przed stratami. Ukazuje się wiele publikacji poświęconych badaniom tego problemu. W niniejszej pracy przedstawiono proponowane w literaturze metody oraz przeprowadzono dyskusję najważniejszych aspektów wstępnej obróbki chemicznej próbek materiałów naturalnych, w procesie oznaczania śladowych zawartości rtęci.

Omówiono wpływ różnych składników, obecnych w roztworze próbki, na wyniki oznaczeń rtęci techniką zimnych par atomowej spektrometrii absorpcyjnej.

The analytical procedures connected with the determination of traces of mercury are rather specific, resulting from the properties of this element. Mercury, a metal with high vapor pressure at normal conditions, distinguishes itself by high chemical activity and an ability to be incorporated in a great number of different compounds, which show diverse chemical and physical properties and dissimilar environmental and biological behaviour.

In the environment, mercury can exist in the elemental state Hg(0), as inorganic ions Hg(I) and Hg(II), as well as in the form of organometallic compounds. The last named substances are formed directly in nature by some biological agents (bacteria, phytoplankton and the like). It is well known that mercury ions show a tendency to form complex compounds both with organic and inorganic ligands (humic acids, chloride ions and other) [1–3]. The ability of mercury(II) ions and organomercury cations to react with sulfhydryl (–SH) groups is accountable for the bioaccumulation of mercury and its toxicity towards living organisms resulting in irreversible genetic changes. Mercury toxicity depends on the form of compound in which this element enters an organism. Organomercury compounds with a short alkyl chain (methyl- or ethylmercury) are the most toxic ones. The stability of these compounds in a biological environment and their good solubility in lipids contributes to the easiness of which they migrate within an organism and to their ability to accumulate in a tissue [4–9].

Mercury is present in all parts of the environment to which it is released from natural resources, creating geochemical background. Its presence in the environment is also a result of human activity since this element and its compounds are used in industry and agriculture [2,3,5,10]. The possibility to contaminate the environment above the allowable limits, as a result of human activity, necessitates monitoring of the concentration of mercury and its compounds in all parts of the environment. Due to chemical and physical properties of this element and its compounds, as well as their low concentration levels at which they are already burden to the environment, the analysis of different biological and environmental samples to determine mercury concentration is a complicated task requiring knowledge, experience and familiarity with the specifics of mercury analysis.

Different analytical techniques are used for mercury determination: atomic absorption spectrometry with electrothermal atomization (ET AAS) [11,12], nuclear magnetic resonance (NMR) [13], gas chromatography with capillary columns (CG-GC) [14,15], atomic fluorescence spectrometry (AFS) [16], inductively coupled plasma atomic emission spectrometry (ICP–AES) [17], inductively coupled plasma mass spectrometry (ICP–MS) [18,19] and cold vapor atomic absorption spectrometry (CV AAS) [20–22] and CV AFS [23–25]. Each of these methods has its own specifics and creates different problems but for most of them chemical pretreatment of a sample is necessary.

This paper reviews the most frequently used mineralization methods of different natural materials. An attempt was made to show what factors are responsible for the effectiveness of different methods. Some problems, which can appear during the analytical process of mercury determination using CV AAS, will also be presented. CV AAS is characterized by high sensitivity, selectivity, simplicity and relatively low costs and is the most frequently used method for mercury determination in various materials. Some factors influencing the reliability of the results and the ways to avoid interferences will also be discussed. This paper can be helpful in finding the appropriate method for the sample preparation and total mercury determination in materials of natural origin.

THE METHODS OF CHEMICAL PRETREATMENT

For the quantitative transfer of mercury from materials of natural origin into a solution, wet mineralization with the use of oxidizing agents is commonly used. High volatility of mercury itself and its compounds excludes the use of dry mineralization. One exception is combustion of a sample, especially coal sample, in a closed vessel and in the oxygen atmosphere [26].

The process of wet mineralization is carried out both in open as well as in closed pressurized devices conventionally heated or using microwave energy. As a mineralization medium can be used different oxidizing agents as well as their mixtures. Usually acids like HNO_3, H_2SO_4, HCl or their mixtures of diverse component ratios are applied. Sometimes the oxidation is supported by additional oxidizing agents such as: H_2O_2, $K_2S_2O_8$, $KMnO_4$ and $K_2Cr_2O_7$ or weakened by the use of diluted acids.

The selection of appropriate oxidizing agents and conditions of mineralization process can be of great importance for obtaining reliable results of total mercury determination in samples of natural origin.

Nitric acid medium

The main and the most commonly used agent for oxidizing of organic matrices is nitric acid. This agent is used on its own or in the mixture with other oxidizers. In the case of the analysis of traces or ultra-traces of mercury when sample contamination can be a hazard it is important to limit the number and amount of reagents used during pretreatment. That is why it is necessary to know whether the use of sole nitric acid will guarantee a quantitative transfer of mercury present in samples of natural materials into solution as mercury(II) ions and preparation of an analytical solution free from components interfering with instrumental measurements. And if it is possible, what conditions have to be fulfilled. The research into this problem was conducted several times but the results are equivocal.

Nitric acid, one and only, seemed to be effective enough for the mineralization performed in a closed, pressurized devices using microwave energy. This type of mineralization was used with success by Jędrzejczak *et al.* [27] to determine mercury in plant and food samples of plant origin. The authors claim that the proper selection of mineralization parameters guarantee a complete decomposition of organic matrix without any loss of the analyte. The mineralization with the use of microwave energy and nitric acid only was also effective enough for the determination of total mercury in bone samples [28]. A complete mineralization of different reference standard materials (plant, animal tissue and sediments samples) using dilute (3+2 v/v) nitric acid was achieved by Ombaba [29] in a high-pressure microwave device. Tahan *et al.* [30] obtained the results being in good agreement with the certified value after mineralizing of tuna fish tissue samples (NIST RM 50) in a closed system using microwave energy. Gulmini *et al.* [31] proved that nitric acid is sufficiently effective for the mineralization of sediments in a closed microwave system. The authors gave no notice of any interferences during mercury determination by CV AAS for the samples prepared using the described method.

Nitric acid alone was use as an oxidizing agent when the mineralization is being performed in closed, Teflon digestion bomb heated in a conventional way. This method was used by Welz *et al.* [12,32] for the mineralization of marine biological tissues for subsequent mercury determination by ET AAS or CV AAS. The mineralization was carried out at 160°C or 140°C. The authors claim that the method used does not assure a complete destruction of an organic matrix but makes it possible to quantitatively transfer mercury to a solution. No interferences during the analyte determination were found. In a medium of sole nitric acid at 170°C, using a pressurized container, the decomposition of hair samples was performed [33]. In a teflon bomb at 140°C soil samples [34] as well as samples of sediments, in a closed quartz container [31] were mineralized. The authors of the latter paper did not found considerable differences in the results of mercury determination when samples were mineralized using microwave energy and when samples where mineralized using a conventional heating.

The analysis of the above mentioned paper enables us to conclude that when a mineralization process is performed in closed, pressurized devices heated by microwaves or in a conventional way nitric acid alone is effective enough as an oxidizing agent and can be used, with success, for preparing various samples of natural origin for mercury determination. However some researchers demonstrate the necessity for using more complicated oxidizing media to mineralize samples of natural materials. It is therefore interesting to find out in which cases it is necessary to increase the oxidizing potential of the medium by using additional reagents.

The use of two oxidizing agents

When a sample of natural origin is mineralized using two oxidizing agents, in most cases, the principal one is nitric acid. However the authors of the papers mentioned below claim that to achieve complete decomposition of samples investigated by them it was necessary to use an additional oxidizing agent. It has to be pointed out that the need to use two oxidizing agents suggest those who conducted a mineralization in closed systems as well as those who used open containers.

Tahan *et al.* [30] who among others successfully used sole nitric acid for the mineralization of lyophilized tuna fish samples (NIST RM 50) with microwave energy found out that the mineralization of the same material using nitric acid but in a high-pressure reactor heated by convection at 130°C does not result in full decomposition of the organic matrix and does not ensure quantitative determination of mercury. To achieve a complete destruction of organic substances, which cause interferences during the process of mercury determination, it was necessary to use chloric(VII) acid as an additional oxidizer. Two oxidizing agents: nitric acid and hydrogen peroxide were also used by Samanta *et al.* [35] while performing mineralization of various standard reference materials in a closed Teflon device.

Woller *et al.* [36] used with success extractive separation of mercury from sediment samples, including standard reference materials (PACS-1, NRCC, IAEA-356, S19), with nitric acid and hydrogen peroxide in an open microwave system. The authors claim that the correct determination of mercury depended on the amount of a sample when the same conditions were used for all samples.

The effectiveness of two-component mixtures of nitric acid and hydrogen peroxide as well as mixtures of nitric and sulfuric acid in an oxidation process of an organic matrix of biological samples were also investigated by Adeloju *et al.* [37]. The results of their investigation are more interesting because of the fact that the mineralization was performed in an open system at low temperature (90°C), using a conventional heating. The authors obtained results, which were in agreement with certified concentration of mercury in biological samples (fish, horse's kidney, bovine liver) and were able to recover all inorganic mercury and mercury incorporated in organic compounds.

Also Landi *et al.* [38] performed the mineralization of plant samples in an open system using a mixture of potassium dichromate and sulfuric acid as oxidizing agents. The process was performed under reflux at 170°C. It is interesting that the authors desist from using nitric acid for the mineralization of samples avoiding the formation of nitrogen oxides, which appear when nitric acid is used.

The use of three oxidizing agents

In some cases even the use of two oxidizing agents was not sufficient to achieve full mineralization of an organic matrix. Golimowski *et al.* [39] performed the mineralization of fish samples in a Teflon bomb in the presence of such oxidizing agents as mixture of nitric and chloric(VII) acids or mixture of nitric and sulfuric acids at 120°C. However to achieve full oxidation of organic interferants they additionally irradiated the samples with ultraviolet light in the presence of hydrogen peroxide. It has to be stressed that mercury was being determined by an anodic stripping voltammetric technique (ASV). This technique requires a complete oxidation of all organic components of a matrix because the dissolved organic compounds strongly influence the results of voltammetric measurements.

Tinggi *et al.* [40] investigated the effectiveness of nitric acid and various oxidizing mixtures for the decomposition of marine biological materials in a microwave oven. The digestion was carried out using only 50% (180W) of microwave power. In this conditions the use of sole nitric acid, mixture of HNO_3 and H_2O_2, as well as a mixture of HNO_3 and H_2SO_4 did not result in complete destruction of an organic matrix. The results of mercury determination were too low and different for the different decomposition methods. Total digestion of samples and the correct results of mercury determination were achieved only when a three-component mixture $HNO_3/H_2SO_4/H_2O_2$ or HNO_3 /H_2SO_4/HCl were used.

The necessity to use a mixture of three oxidizing agents $HNO_3/H_2SO_4/H_2O_2$ was confirmed also by Lamble *et al.* [41]. They performed digestion in an open microwave system using microwave energy with power of 20 W. Performing the optimization of the digestion procedure for a reference standard material DORM–2 (Dogfish muscle) they found that the results of the analysis depend not only on the kind and number of oxidizing agents but also on such parameters as the power of microwaves and digestion time. Similar conclusions can be drawn out from the research carried out by Mohd *et al.* [42].

More complexed oxidizing mixtures

The information presented above leads to a conclusion that the necessity to use more complicated oxidizing mixtures arises from the conditions at which the process is to be carried out. The temperature seems to be the most important factor. The lower is the temperature of mineralization, the higher should be the oxidizing potential of the system and this requires the use of multicomponent oxidizing mixtures. This conclusion was confirmed by the results of Mc Mullin *et al.* [43]. They mineralized hair samples at low temperature (50–110°C) in an open system under reflux using a multistage procedure. Full mineralization of the organic matrix, without mercury loss, was achieved only when four oxidizing agents were used: HNO_3, $HClO_4$, H_2SO_4, and H_2O_2.

Low temperature and multicomponent oxidizing mixtures were also used to digest water samples. However, the composition of the mixtures is different from the one previously described. This difference is probably caused by the kind of a matrix and a chemical form in which mercury is present in this material. The most commonly used oxidizing agent in this case is potassium manganate(VII) ($KMnO_4$). Sometimes it is replaced by potassium peroxydisulfate(VI) ($K_2S_2O_8$) or, what is more common, these reagents are used together in with an acid mixture [44–48]. The effectiveness of this composition is justification for its use. In the presence of HNO_3 and H_2SO_4 manganate(VII) oxidizes sulfides and $K_2S_2O_8$ oxidizes organic components of the sample

[49]. Moreover the results of a comparative research conducted by Baxter *et al.* [22] show that the use of a mixture of acids in connection with other oxidizing agents ($HNO_3 + H_2SO_4 + KMnO_4 + K_2S_2O_8$) at low temperature of 50°C [50,51] gives better results than the use of HNO_3 only in a pressure method (200 kPa 120°C) [52]. The results of Uchino *et al.* [44] and Hanna *et al.* [45] confirmed the efficiency of multicomponent mixtures containing, besides acids, additional oxidizing agents in digesting water samples at 100°C. In the case of water samples analysis for mercury determination, high temperature and pressure is not necessary. The use of additional oxidizing agents makes effective digestion at mild conditions possible without potential risk of mercury loss [53].

In summary, the effectiveness of a digestion process of samples of natural origin for the subsequent mercury determination depends on many different factors. They are: the oxidizing potential of the system, process conditions, a kind of material and a sample amount. The close connection among these factors is the reason why for obtaining desired results it is necessary to match the oxidizing potential of the medium to the condition of digestion process, kind of analyzed material and sample amount. In the case of most samples of natural materials the use of high pressure devices and maximal microwave energy, giving the possibility to reach high digestion temperatures in short time, leads to total destruction of an organic matrix by sole nitric acid. This digestion method does not require the use of additional oxidizing agents for the quantitative transfer of mercury into a solution and to remove the sample components causing interferences. Similar results can be obtained in pressure Teflon bombs heated in a conventional way [54]. Using this device it is possible to increase digestion temperature to 170–180°C. At this temperature nitric acid is efficient enough to digest almost an entire organic matrix and transfer mercury to a solution as mercury(II).

However, when the digestion process is carried out in a closed pressure devices using microwave energy of low power or heated in a conventional way to a temperature lower than necessary for the destruction of organic matrix by sole nitric acid, it is necessary to use additional oxidizing agents. In this case to obtain acceptable results of mercury determination it is important to optimize the process parameters such as time and temperature, which depend on the kind of analyzed material and sample amount. Many authors [21, 35, 55-57] give preference to the digestion in closed vessels. This digestion mode prevents from the loss of mercury and also from the loss of oxidizing agents. It also prevents the sample from being contaminated by the components of laboratory atmosphere.

The use of open systems for the digestion of natural materials increases the risk of mercury loss. How much of mercury is lost depends on the oxidizing strength of the medium and the temperature. Suitably high oxidizing potential of the medium is necessary not only for the oxidation of organic matrix but also, what is equally important, to preserve mercury at the second oxidation level. The deficit of oxidizing agents in comparison to the stoichiometric amounts, can create conditions promoting the reduction of mercury(II) to elemental mercury and can lead to the loss of the latter as a consequence of its evaporation from the reaction medium. To avoid this undesired phenomenon it is necessary to use an excess of oxidizing agents and use proper protection against their loss and the loss of mercury in open systems. Despite some risks, digestion in open systems heated by microwaves or by convection leads to correct results of mercury determination in materials of natural origin. In these conditions the use of nitric acid only is not sufficient to obtain total destruction of an organic matrix. The oxidizing potential of nitric acid in the conditions of digestion process at normal pressure is too low for the oxidation of some of the components of natural samples [58]. The increase of nitric acid excess and lengthening of the heating time did not lead to better results. Full digestion and quantitative transfer of mercury, as mercury(II), into solution is only possible when additional oxidizing agents are used.

The analysts making a decision on the selection of oxidizing agents has to be aware of both advantages and the risks, which are connected, with the use of these agents.

The introduction of sulfuric acid and chloric(VII) acid to the reaction mixture causes the increase of the oxidation potential of the system and makes it possible to reach higher digestion temperatures. However, a significant increase in temperature, especially when an open system is used, can lead to loss of mercury. Moreover, the use of sulfuric acid, even in a mixture with nitric acid, can cause carbonization of some organic matrices [59, 60]. Hence when sulfuric acid is to be used it is necessary to dilute the reaction mixture with water [38]. On the other hand the reaction of organic substances with chloric(VII) acid can be very exothermic and leads to an uncontrolled increase in temperature, sometimes even to ignition of a sample, especially in the case of bigger samples containing a great deal of organic material. That is why chloric(VII) acid should be used only in the second stage when most of the organic matrix was digested by nitric acid.

The role of hydrochloric acid, which is used during sample chemical pretreatment as an auxiliary reagent, is worth noticing. This acid can on one side play the role of an agent stabilizing mercury(II) ions forming a stable chloride complex $[HgCl_4]^{-2}$ [61], on the other hand together with nitric acid it formes a mixture capable of destroying organic as well as inorganic sample components. Nevertheless the use of hydrochloric acid in a mixture with nitric acid and sulfuric acid results in the appearance of undesirable phenomena, which are descriebed more closely farther on.

When analyzing natural sample to determine mercury there is no need to use hydrofluoric acid in the sample digestion process. Mercury has a large ionic radius and do not form natural compounds with silicon [62].

In the digestion process of samples of natural origin hydrogen peroxide is used very frequently. The oxidizing potential of this reagent is not high enough to digest materials rich with organic components [59] and that is why it can be used as an additional oxidizing agent. Its effectiveness depends on the time point at which it is introduced to the reaction mixture. Better results can be obtained when hydrogen peroxide is used during the second stage when part of the organic matrix was oxidized with nitric acid [36,41]. Since this reagent is thermally unstable it should be added in small amounts to the reaction mixture what can cause some technical problems during the digestion process.

Some problems can also appear when potassium manganate(VII) is being used for the digestion purposes. Potassium manganate(VII) in the presence of some organic substances, even in an acid medium, is reduced to manganese(IV) oxide, which is a solid [63,64]. The formed precipitate can hinder complete oxidation of an organic matrix and diminish the effectiveness of mineralization process and that is why potassium manganate(VII) can be used only when a sample does not contain a great deal of organic substances.

It is advantage to use potassium dichromate. Although it has a lower oxidizing potential, it is possible to avoid problems connected with the use of such oxidizing agents as potassium manganate(VII) or hydrogen peroxide. When the reaction is carried out in the presence of sulfuric acid, without otherwise commonly used nitric acid, it is possible to avoid interference from nitrogen oxides in the process of mercury determination by CV AAS. However, the analysts have to keep in mind the risks connected with the use of sulfuric acid, which were described earlier.

The introduction of additional oxidants can lead to an increase in a blank value what is especially undesirable when the concentration of mercury is at the ultra-trace level. In a situation like this it is necessary to limit the number of reagents and use more drastic digestion conditions or make use of special procedures to purify the reagents in order to obtain the analytical blank at an acceptable level.

The methods for sample preparation, described above, are related to the total mercury determination. However more and more frequently to evaluate the threat from mercury presence in an environment a speciation analysis is performed with the purpose to determine the concentration of separate mercury forms. To achieve this goal it is necessary to isolate, from the investigated material, different forms of an analyte in an unchanged form, scrupulously separate them from the matrix components causing interferences, avoiding losses and/or contamination. Because of this, the speciation analysis requires other sample pretreatment methods and is connected with other than described analytical problems. On account of the complexity of the speciation analysis and diversity of the methods used and their multistage character, a detailed presentation of these methods and their wider description is beyond the scope of this paper.

THE ANALYTICAL PROBLEMS CONNECTED WITH MERCURY DETERMINATION BY CV AAS

The process of mercury determination by CV AAS consists in the reduction of mercury(II) ions to elemental mercury using one of two reducing agents: tin(II) chloride or sodium tetrahydroborate, and measuring the absorbance of the produced mercury vapors. This method is not free from some analytical problems despite its simplicity. The results can be influenced by some components of the sample solution originating from the matrix of the investigated material or introduced during the chemical pretreatment. Organic and inorganic components of the analyzed sample such as: water vapors, halide ions (especially iodide ions), noble metals, selenium and tellurium as well as amino acids or complexing agents present in the sample solution can be the cause of interferences during the measurement. These factors suppress the analytical signal as a result of their reaction with the analyte or strengthen it as a result of intrinsic absorbance of an interferant [65–72].

The scope of the interference caused by organic components of the sample matrix depends on the effectiveness of the mineralization process. The selection of an appropriate mineralization method for a particular sample allows for complete elimination of this type of influence.

More complicated problem are the interferences originating from inorganic sample components. The potential interferants in the process of mercury determination by CVAAS are ions of those elements which, together with mercury, undergo reduction to the elemental form or form unstable hydrides during this process. In this form interferants can react with mercury vapors, eliminating mercury from the measuring process, by adsorption on a surface (Pt, Pd), formation of amalgams (Cu, Ag, Au) or chemical compounds (Se, Te) [67]. The scope of these interferences depends on the kind and concentration of interferants as well as the methodological details for mercury determination such as: the kind of a system, kind of a reducing agent, the use of preconcentration *etc.* [65,68–72]. Basically the researchers agree that the use of each of two most frequently used reducers ($SnCl_2$, $NaBH_4$), from the point of view of the interferences, is both advantageous and disadvantageous. When $SnCl_2$ is a reducing agent the interferences caused by heavy metals are less frequent. Whereas $NaBH_4$ on one hand causes an increase in interferences, connected with the presence of copper, and significant interferences from elements forming hydrides, on the other hand it limits the interferences from iodide and selenium ions [65,69]. These effects probably result from the different ability of reducers to transform an interferant into an active elemental form, which is responsible for the interferences during mercury determination (what was mentioned earlier). The conclusion resulting from this is that the proper selection of a reducing agent, taking into account the composition of a sample matrix, can reduce the disturbing actions from inorganic components.

It is worth noticing, however, that the selection of a reducing agent is linked with the mercury concentration in the investigated samples. The use of sodium boron hydride increases the level of an analytical blank and this is a reason why this reducing agent should not be use for mercury determination when the concentration of mercury is below 10 ng l^{-1}. In this case the use of tin(II) chloride is preferable [22].

The influence of foreign components on the results of mercury determination can be eliminated to a great extent by separating the analyte from the investigated solution forming an amalgam with gold or platinum. The absorbance of mercury is measured after its thermal desorption from the amalgam. This manipulation allows the simultaneous concentration of mercury [21,30,73,74]. The use of two stage amalgam forming procedure makes possible to avoid interferences caused by water vapor and organic compounds [75]. According to more recent approach mercury is being concentrated directly in an absorption cell. This procedure makes possible to lower the detection limit down to the ppt level and to determine absolute content of mercury at the level of 0.1 ng. The method consists in combining vapor generation techniques with their deposition in graphite furnace cuvettes. For this purpose Au-coated graphite furnace cuvettes [76,78], or Pt-lined graphite tubes [79] can be used. Mercury determination is performed using ETAAS method.

The reliability of the analytical results also depends on the quality of the reagents used during chemical pretreatment of the analyzed samples as well as the interferences from the substances produced during the mineralization process.

The sensitivity of mercury determination by CVAAS can also strongly depend on the kind and concentration of acids present in the standard solutions as well as in the sample solutions [37,61,80–83]. This problem increases in importance when during the mineralization process different acids, which can be present in the analytical sample in unknown amounts, are used. The results of the investigation into this problem [37,80,81] showed that the analytical signal from mercury increases with the increase of sulfuric acid concentration in a sample and decreases, although less strongly, with the increase of nitric acid concentration. The change in the ratio of components in the mixture of $HNO_3 + HClO_4$ and $HNO_3 + H_2SO_4$ is of lesser importance. Hydrochloric acid stabilizes mercury(II) ions and at concentration lower than 2% does not influence the absorbance signal from mercury. The results of investigations show that to obtain proper results of mercury determination by CV AAS it is necessary that the concentration of acids in the analytical samples of the investigated materials is identical with the concentration of these acids in the standard solutions, especially when a mixture of nitric and sulfuric acids is used in the mineralization process.

Similar conclusions can be drawn out of the work of Bulska *et al.* [82], the authors also found, that the character of the influence of acids, present in the sample solution, on the signal from mercury depends on the kind of reducing agent, which was used to generate mercury vapors. When the reducing agent was $SnCl_2$, it was observed that the analytical signal from mercury was suppressed when HNO_3 were present at concentration 3 mol l^{-1}. Similar effects were obtained when HCl or aqua regia were present at the concentration as small as 0.5 mol l^{-1}. The use of $NaBH_4$ as a reducer makes possible to obtain a signal which is independent of the kind and concentration of an acid used when its concentration is not higher than 4 mol l^{-1}. The conclusion from this finding is that it is possible to determine mercury in a solution, obtained as a result of digestion, without a strict control of acidity.

The result of mercury determination by CV AAS can also be influenced by nitrogen oxides present in analytical samples. This problem was raised by Adeloju et al. [80] who found out that the addition of hydrochloric acid to the mixture of nitric and sulfuric acids caused very strong interferences from nitrogen oxides leading to the disappearance of the analytical signal from mercury. The interferences caused by nitrogen oxides can be especially important when samples of natural material are analyzed. These compounds form always during the mineralization of an organic matrix when nitric acid is used as an oxidizing agent. To a certain extent they remain in the analytical sample solution and their removal requires the use of special methods. The interference by these compounds the authors explain as an oxidizing effect on the ions of reducing agents Sn(II) concentration which becomes too low to guarantee quantitative reduction of mercury(II) to the elemental state. The increase of the amount of a reducing agent can in this case be one of the means to remove this disturbing influence. Other methods to eliminate the mentioned interferant such as purging the sample with argon after treating the sample with ultrasounds [27], leaving the solution till the next day and then the use of a chemical reaction with urea and amidosulfonic acid [80].

It is worth noticing that despite the common use of nitric acid for the digestion of samples of natural origin, the interferences caused by the presence of nitrogen oxides in the analytical samples are mentioned by few researchers. Those who mention them, usually do not comment it. Analyzing many papers, we came to the conclusion that the appearance of interferences from nitrogen oxide during mercury determination is closely connected with the concentration of this interferant in a measured sample. The contents of nitrogen oxides in the analyzed solution depends on many factors such as: the kind of analyzed material, amount of acids used in a digestion process, amount of a sample, digestion method, sample dilution *etc*.. As a result, in many cases the concentration of nitrogen oxides at certain conditions can not be higher than a maximum value above which the interferences are observed. According to the interpretation of effects proposed by Adeloju *et al.* [80] also the kind and concentration of a reducer used, as well as the time between the end of mineralization process and the instrumental measurement can be of importance.

The results of mercury determination by CV AAS in samples of natural origin depend on the chemical form in which this element exists in the analytical sample. None of the earlier mentioned reducing agents is able to quantitatively reduce mercury incorporated in organic compounds. Although some authors [83,84] suggest that the use of sodium boron hydride in combination with copper makes possible, in some cases, to determine total mercury without foregoing oxidation procedure, but it was not confirmed by other authors [22,53,85]. Although sodium boron hydride is a stronger reducing agents than tin(II) chloride it also does not reduce quantitatively all mercury-containing organic compounds [22,53]. Thus for the quantitative determination of total mercury in samples of natural origin, no matter what kind of reducing agent was used, it is necessary to convert all mercury in to mercury(II).

CONCLUSION

The direct determination of mercury traces in materials of natural origin is impossible in most cases. To liberate mercury from a sample and to convert it quantitatively into a form compatible with the instrumental technique used, as well as to remove matrix components interfering with the mercury analytical signal, it is necessary to subject the samples to chemical pretreatment.

Various mineralization methods can be used for this purpose. In order to obtain reliable results it is necessary to perform this process in a way permiting a total destruction of organic matrix and decomposition of organomercury compounds and at the same time preventing mercury losses. It is worth mentioning that the destruction of mercury containing compounds and the conversion of mercury contained in samples of natural origin into mercury(II) not always requires extreme conditions. Even when the mineralization of the organic matrix is incomplete quantitative transfer of mercury to solution as mercury(II) is possible. However, there can be problems with interferences during the instrumental measurements caused by nonoxidized components of the organic matrix. The scope of this problem depends on the measuring technique used. That is why choosing a method of chemical pretreatment the analyst has to take into account the character and composition of a sample as well as the properties of the analyte and specifics of the instrumental technique. In any case the correctness of the choice has to be checked using alternative mineralization methods and standard reference materials.

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Received February 1999
Accepted January 2000