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AAS-Determination of Mercury in a marine biological reference material after wet ashing by means of microwaves. Preliminary results

André VEGLIA

Centre Scientifique de Monaco, 16 boulevard de Suisse,
98030 Monaco Cedex (Principauté de Monaco)

The application of microwaves to the mineralization of marine biological materials for the purpose of the determination of mercury has been investigated.

The digester "Microdigest - 300" produced by PROLABO was tested. This apparatus consists of a source of microwaves (magnetron), a waveguide, a borosilicate glass round-bottomed flask which contains the sample (capacity 30 ml) and a water circulation system which absorbs the excess of radiations. The long neck of the flask facilitates the reflux of water. The flask is covered with a teflon-lined steel cover. Nitric oxide vapours go out through a small hole in the cover.

The method was tested by using the reference material MA-M-2/TM (lyophilised mussel tissue) issued by the IAEA. The mercury content of this material was certified on the basis of the results of various methods of analysis obtained in a laboratory intercomparison (IAEA, 1985).

65% nitric acid (analytical grade, mercury-free) was used as oxidizing agent. 30% hydrogen peroxide (analytical grade) was occasionally added. Mineralization tests were done under varying operating conditions (amounts of reagents, microwave energy and duration of mineralization). About 800 mg of reference material were mineralized each time. In none of three separate attempts could the material be completely dissolved and the sample solutions were filtered before the determination of their mercury contents by cold-vapour atomic absorption spectroscopy (HATCH & OTT, 1968).

Results given by this method were compared to those of a classical method of mineralization (wet-ashing by HNO3 under normal pressure and reflux) and to the certified value for the mercury concentration in this material (table 1). The confidence interval of the results given by the classical method overlaps the confidence interval of the certified value while results of the microwave mineralization are significantly lower than this value (they are about 20% too low).

The mineralization by microwaves was obviously less complete than the mineralization by the classical method. Incomplete mineralization rather than loss by volatilization is , therefore, the most probable explanation for these low results. An increase of microwave energy was not satisfactory since it produced a strong evaporation of the acid solution. A modification of the cover of the apparatus in order to fit a sufficiently long Vigreux column on the top of the mineralization flask is suggested . Such a system would make possible to increase the microwave energy and to obtain a more complete mineralization.

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Table 1
Mineralization of MA-M-2/TM
by microwaves and by the classical method
(Comparison of results)

Consensus value (a) (µg.g-1)	Attempt N°	Found value (µg.g-1) Mineralization by microwawes (b)	Classical method (c)
0,95 µg.g-1 (0.85 - 1.06)	1	0.78 ± 0,06	0,86 ± 0,07
	2	0.78 ± 0,06	
	3	0,73 ± 0,06	

(a) Recommended by IAEA, 1985
(b) Confidence intervals correspond to a 0.95 probability level and were computed from 4 different measurements of the same solution
(c) Mean value of 5 different mineralizations ± confidence interval corresponding to a 0.95 probability level.

Speciation of Mercury by cold vapor atomic absorption spectrometry : effect of several reduction mediums on inorganic and organic Mercury

A. PASTOR GARCIA and J. MEDINA ESCRICHE

Department of Analytical Chemistry, University of Valencia,
Dr Moliner 50, Burjasot, Valencia (Spain)

The toxic and accumulative character of methyl, ethyl and phenyl-Hg and its high proportion against inorganic-Hg in many environmental samples makes its determination to be more useful than total-Hg determination. For this purpose it is important to get analytical and enough reliable procedures for the speciation of Hg as inorganic as organic forms. Classical procedure for the determination of organomercurials is carried out by GLC. By other hand, recently have been developed procedures for their speciation by CVAAS on the basis of the diference between the reducing effect of Sn(II) and $NaBH_4$ in several mediums. However, their reducing capabilities depend on as chemical as instrumental variables, therefore their applications to samples have to carry out with restrictive conditions. Furthermore, the reduction of inorganic and organic-Hg by the action of a reducing system depends on the kinetic of the process, therefore the reliability of the results depends also on it.

In this work the reducing power of these agents is show through the reduction percentage of each organic specie respect to the signal given by inorganic-Hg. With this, we want to get an systematic and overall information about the behaviour of these agents in order to optimize the determination of the several forms of Hg.

We have used the following solutions: 0.4 µgHg/ml of $HgCl_2$, CH_3HgCl, C_2H_5HgCl, C_6H_5HgCl, all of them prepared daily from a 100 µgHg/ml stock solutions; $SnCl_2.2H_2O$ 5%+HCl 10%; $SnCl_2.2H_2O$ 5%+ $Cd(NO_3)_2.4H_2O$ 1%+HCl 10%; cysteine 1%; NaOH 45%; $NaBH_4$ 3%+NaOH 1% and HNO_3 20%+$K_2Cr_2O_7$ 1%.

The determinations of Hg were carried out with a Perkin-Elmer 5000 AAS equipped with a recorder 561, Pye Unicam Cold Vapor Kit with an absorbance cell (150 mm pathway) and a peristaltic pump for the reductions with Sn(II) in closed system, and a Perkin-Elmer Mercury Hydride System MHS-10 for the reductions with $NaBH_4$ in open system.

In table 1 are shown the percentages of reduction got when added 10 ml of reducing agent (Sn(II) or Sn(II)+Cd(II)) to 20.5 ml of sample (0.2 µg Hg) + 10 ml HCl (1:10) or 10 ml de NaOH (45%). The three organic forms show a low response in acid medium with and without Cd(II), not easily attributable to impurities of inorganic-Hg; in alkaline medium the reduction is total for phenyl-Hg while for methyl and ethyl-Hg, although high, does not reach to be quantitative, however it is higher than reported by other authors in these mediums (1).

Table 2 indicates the percentages for the former mixtures in presence of 1 ml cysteine. A general decrease of the reducing power is observed, getting a whole reduction only for phenyl-Hg with an alkaline medium in presence of Cd(II). In alkaline medium and without Cd(II), the reduction of organomercurials is remarkable and higher than reported by other authors (2,3), who pointed out that only the inorganic-Hg gives signal.

The presence of cysteine delays the reduction, in such a way that the signal increases against time specially for ethyl-Hg. That means, that when the time of measure increases also increases the percentage of reduction.

From eight mediums tested, only Sn(II) in acid or alkaline medium, without Cd(II)+cysteine, offers the most suitable values to carry out the speciation, although we have not found any medium which could offer a null reduction for the organomercurials. Addition of Cd(II) in alkaline medium improves slightly the recovery of methyl-Hg (4). Furthermore, these mediums without cysteine offer the highest sensibility.

Table 1	Sn(II)		Sn(II)+Cd(II)	
	HCl	NaOH	HCl	NaOH
Methyl-Hg	2.9	92.0	5.9	96.6
Ethyl-Hg	2.7	98.6	4.1	81.8
Phenyl-Hg	2.5	101	3.9	101
Hg(II)sens. (μg^{-1})	0.78	1.08	0.84	1.05

Table 2	Sn(II)		Sn(II)+Cd(II)	
	HCl	NaOH	HCl	NaOH
Methyl-Hg	7.4	12.5	3.4	83.5
Ethyl-Hg	0.7	59.7	3.4	79.5
Phenyl-Hg	2.3	32.0	1.2	100
Hg(II)sens. (μg^{-1})	0.48	1.05	0.43	1.04

Table 3 show the percentages of reduction got when $NaBH_4$ solution was added to 5.5 ml of sample (0.2 µg Hg) + 5 ml of any solution to give suitable medium. The reduction is only quantitative in presence of $K_2Cr_2O_7$ in contrast with the values of 84% (methyl and ethyl-Hg) and 50% (phenyl-Hg) given by Oda and Ingle (5). If we consider methyl-Hg the main compound in samples could be carried out the speciation between this and inorganic-Hg by means of reductions with $NaBH_4$ in HNO_3 medium and later measure of methyl-Hg by addition of $K_2Cr_2O_7$.

Table 3	HCl 1.7%	HNO_3 10%	HNO_3 10%+$K_2Cr_2O_7$ 0.5%
Methyl-Hg	16.3	1.9	99.7
Ethyl-Hg	13.4	8.1	99.5
Phenyl-Hg	34.5	24.7	99.9
Hg(II)sens. (μg^{-1})	1.48	1.48	1.49

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