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Detection of Mercury Residue in Aquatic Products Using Direct Sampling

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The method was developed for rapid detection of mercury residue in aquatic products using direct sampling. Chemical pretreatment like digestion was not necessary in this method, but only simple pretreatment by physical way is needed. The results showed that the limit of detection was 6.3 μg kg^{-1}, rate of recovery was 95-105 %, linearly dependent coefficient is 0.9995 and the relative standard deviation of detected precision was 5.01-6.77 %, while the relative deviation compared with standard value of precision is 0.397 %. With the advantages of safety, convenience, environment-protection, accuracy, high precision and low limit of detection, the method is obviously advantage compared with microwave digestion- atomic fluorescence spectrometry and micro digestion-inductive coupled plasma mass spectrometry.

Keywords: Mercury residue, Rapid detection, Aquatic products, Direct sampling, Solid automatic analyzer of mercury.

INTRODUCTION

Mercury is one kind of toxic heavy metal, which is considered to be introduced to human being mainly from aquatic products[1-6], it threatens to human health and safety. Currently, the detection methods of total mercury in foodstuff are mainly atomic fluorescence spectrometry (AFS), cold atomic absorption spectrometry (CAA), inductive coupled plasma mass spectrometry (ICP-MS), dithizone colourimetric method (DSPM), *etc.*[7-21]. However, the above mentioned methods have defects such as high consumption of reagent, low detection precision, complex operation, time costing, bad reproducibility and slow detection.

At present, the pretreatment of samples used for detecting total mercury are mainly high pressure digestion and microwave digestion, of which the operation is complicated and time consuming. Furthermore, mercury is of low boiling point and easy to volatilize, which may cause both analysis deviation and environmental pollution as well as safety and health problems to the operators. To deal with the problems of complicated operation of pretreatment prior analysis of mercury in aquatic products and bad reproducibility, the total mercury contents in aquatic products are to be directly detected by direct sampling using solid automatic analyzer of mercury, which is of no pretreatment, no pollution, rapid, high efficiency and time saving[22].

EXPERIMENTAL

The solid samples were weighed accurately and sent to sampling cell *via* automatic sample injector. The samples were then dried by oxygen flow to be burnt to carbon dioxide and water without production of mercury oxide (mercury oxide resolves in high temperature). The thermal resolved products were send into catalyst furnace after being deoxidized, mercury was deoxidized to mercury atom while mercury steam was brought into amalgamation tube. At low temperature (250 °C), the gold inside amalgamation tube absorbed mercury steam while other gases were exhausted. Subsequently, the temperature of electric stove wire coil outside amalgamation tube promptly rised and the absorbed mercury was released when temperature arrived at a high point (550 °C). The mercury steam was collected by amalgamation tube and co-reacted with the gold fully. After being resolved in high temperature, the mercury content will be resolved at 254 nm of absorption basin by cold atomic absorption spectrometry.

The quartz boat is also named as cell of quartz glass in the experiment, which is melted from silicon tetraoxide at high temperature. With excellent electric performance, its electric resistance equals ten times of normal glass in normal temperature. The dielectric loss to all frequencies is minor, while its insulation performance and pressure resistant tension is high.

HYDRA-C Solid Automatic Mercury Analyzer (U.S. Leeman Technical Co., Ltd), analysis balance (0.1 mg of min. weight) and microwave muffle furnace.

Scallop (GBW10024), Laver (GBW10023), Cabbage (GBW10014) and Chicken (GBW10018). GBW:China standard substance for certified reference material.

The solid sample was pulverized into the granule to pass through sieve of 40-60 mesh. Liquid and paste appearance viscous samples are not necessary to be pretreated. The scallop (GBW10024) was accurately weighed: 0.020, 0.050, 0.080, 0.100, 0.120 and 0.150 g to make the standard curve.

Dry temperature: 250 °C, dry duration: 80s; resolve temperature: 550 °C, resolve duration: 100s; catalysis temperature: 600 °C, catalysis duration: 60s; gold-mercury co-reaction temperature: 600 °C, gold-mercury co-reaction duration: 60s; duration for recording measuring signal integral: 80s; oxygen velocity: 350 mL min^{-1}.

The scallop (GBW10024) was accurately weighed as 0.020, 0.050, 0.080, 0.100, 0.120 and 0.150 g, respectively, in quartz boat, which were individually sent to pyrolyzing furnace by sample injector of mercury analyzer. The compound mercury standard curve of 0.80, 2.00, 3.20, 4.00, 4.80, 6.00 mg L^{-1} was drawn with independent variable of mercury element concentration and dependent variable of absorbance. The spectral intensity of mercury element in blank and test sample was detected successively and the concentration of corresponding group was indicated on the working standard curve. The colourimetric tube of mercury analyzer is consisted of two parts, which are long one and short one. The mercury steam first entered into the long tube, thus the signals in the long tube were read on the instrument in prior. When the absorption value in long tube exceeded 0.8, the instrument automatically switched the input signal to the short tube. Therefore, low content standard curve data and high content standard curve data were, respectively obtained in the long tube and short tube.

The samples with mercury content below 30 ng were collected and put to the sample boat, which were washed, dried and burnt at 500 °C for 0.5 h. The samples of severe reaction and high liquid content must be put into quartz boat.

RESULTS AND DISCUSSION

Linear relation of method and detection limit: In this method, the working standard curve was established based on scallop (GBW10024). It weighs standard reference materials powder successively 0.020, 0.050, 0.080, 0.100, 0.120 and 0.150 g, which were, respectively detected. The peak area finally generates equation of standard working curve as:

$$Y = 181.83x + 5.9333, \quad r = 0.9995 \qquad (1)$$

The blank samples were detected continuously for 11 times to calculate the standard deviation of blank value. As per detected limit.

$$L = ks/b \qquad (2)$$

(in case of 95 % confidence coefficient, k = 3; b was the sensitivity of the method, *i.e*. slope of regression equation). The calculated detection limit was 6.3 μg kg^{-1}.

Precision of method: Different samples of aquatic product were collected to carry out parallel detection for 12 times (m = 15 mg). By optimization with exclusion of the groups of systemic error and mechanical defects, six results of parallel detection were finally collected. The relative standard deviation of six samples was 5.01-6.77 % (Table-1).

Recovery rate of method: The samples of grass carp were detected in parallel. Eleven specimens of grass carp were collected and detected. The standard reference materials of scallop were engaged to execute recovery comparison experiment. The recovery rate was 94-105 % as three times of parallel detection were collected. (Table-2).

Accuracy of detection: Three standard reference materials of laver (GBW10023), cabbage (GBW10014) and chicken (GBW10018) were detected. The results were soundly consistent with value of standard reference material (Table-3).

Comparison with microwave digestion-atomic fluorescence spectrometry and microwave digestion-inductive coupled plasma mass spectrometry

The samples of grass carp and standard reference materials of scallop (GBW10024) were respectively detected by microwave digestion-atomic fluorescence spectrometry (AFS), microwave digestion-inductive coupled plasma mass spectrometry and solid automatic mercury analyzer (Table-4). The relative standard deviation (RSD) among three methods was 0.425-

TABLE-1
PRECISION OF DETECTION (μg kg^{-1})

Samples	Times of detection						Average	RSD (%)
	1	2	3	4	5	6		
Specimen 1 prawn	8.9242	7.4047	8.2738	8.3392	8.0020	8.0739	8.1696	6.0744
Specimen 2 grass carp	11.9160	11.4466	10.2907	10.7944	11.2957	11.1646	11.1513	5.0107
Specimen 3 sea cucumber	12.7607	12.5363	12.9429	11.4486	12.3882	13.7982	12.6228	6.7749

TABLE-2
RECOVERY RATE OF DETECTION

Samples	Value of original (ng)	Value of addition (ng)	Value of detection (ng)	Recovery rate (%)
Specimen 2 grass carp	0.8419	2.0000	2.9900	105.2105
Specimen 2 grass carp	0.8475	2.0000	2.7800	97.6295
Specimen 2 grass carp	0.8910	2.0640	2.7800	94.0782

TABLE-3
ACCURACY OF DETECTION

Standard reference materials	Value of standard reference (μg kg^{-1})	Value detected	Relative detected (%)
Laver (GBW10023)	16 ± 4	15.7429	1.6063
Cabagge (GBW10014)	10.9 ± 1.6	10.8741	0.2376
Chicken (GBW10018)	3.6 ± 1.5	3.6235	-0.6528
	Average	0.3970 %	

TABLE-4
COMPARISON OF METHODS

Samples	Content of mercury (μg kg^{-1})			RSD (%)
	Method 1*	Method 2*	Present method	
Grass carp	10.5871	10.7223	11.1513	5.0106
Scallop	38.9127	39.2109	40.1300	1.3937
Chicken	3.2239	3.3144	3.6235	5.6175

*Method 1: Microwave digestion-atomic fluorescence spectrometry; Method 2: Microwave digestion-inductive coupled plasma mass spectrometry

5.7 %. The detection limit was 0.2 μg kg^{-1}, which is close to the detection limit 0.15 μg kg^{-1} of atomic fluorescence spectrometry. Comparing with atomic fluorescence spectrometry, direct analysis of mercury saves the samples of digestion, reduces the time for analysis. In addition, it is less pollution and loss of mercury as well as less disturbance to detected samples.

Conclusion

The analysis method was developed to rapid detection of mercury residue in aquatic products using direct sampling solid automatic mercury analyzer. With advantages of simple operation and few quantity of sample, it's unnecessary to pretreat the sample with chemicals. Besides, it takes only 5 min to detect each sample. When the aquatic products are detected by solid automatic mercury analyzer, the detection limit is 6.3 μg kg^{-1}, recovery rate is 95-105 %, relative standard deviation of precision is 5.01-6.77 % and relative deviation of accuracy is 0.3970 % comparing to standard reference value. For its safety, convenience, environmental protection, high accuracy, fine precision and low detection limit, it prevails to microwave digestion-atomic fluorescence spectrometry and microwave digestion-inductive coupled plasma mass spectrometry. Therefore, it's applicable for rapid detection of mercury residue in large amount of aquatic products.

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