Construction and Applications of Database for Hair Mercury Contents of College Students

Innovation to an Environmental Monitoring Experiment

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Abstract—**The monitoring experimental item "determination of mercury in human hair" is the important item in environmental monitoring course. Due to the disadvantages of reagent purity and digestion method recommended by reference book widely used, there has been poor accuracy in determining hair mercury contents in environmental monitoring experiments. By improving the digestion of hair samples in this study, accurate mercury contents of hair samples could be obtained. New standard for assessing health risk of mercury is introduced. Database of hair mercury contents and affecting factors is constructed on the base of parameters from questionnaire. Thus the monitoring experiment of hair mercury is changed from a simple determining test to a comprehensive experiment item, integrating sampling, accurate determination, subsequent scientific evaluation and statistical analysis.**

Keywords- environmental monitoring; experiment improvement; process management; comprehensive experiment

I. INTRODUCTION

Environmental monitoring and its experiments are the important practical specialized course for environmental engineering and science, with the important position in environmental related curriculum system [1-4]. The experiment item of determination of mercury (Hg) in human hair, as the only item using the Cold-vapor Atomic Absorption Method, plays an important role in comprehensive training of college students. As "biomarkers" in a broad sense, the hair mercury content can better reflect the mercury exposure of human bodies [5]. Generally, the sensitive population and people eating a large number of fish products have the higher risk of methyl mercury poisoning [6]. For the environmental monitoring, accurate determination of mercury contents in different environmental samples including human hair is of great significance. However, the present college environmental courses introducing Cold-vapor Atomic Absorption Method focus more on classroom theory and less on corresponding experimental operation. Moreover, in the current widespread used experimental teaching materials, it is difficult to obtain accurately the hair mercury content according to "determination of the hair mercury levels" experiment, due to the determining method, reagent purity and so on [7]. In addition, the lack of subsequent analysis and evaluation to the experimental results could not improve the students' interest in participation enthusiasm and accomplish the practice ability training.

This study intends to adopt the optimized method to obtain the accurate data of college students' hair mercury content. On this basis, combining with the questionnaire survey on influencing factors of hair mercury content, the open database for the hair mercury levels of different grades of students could be constructed. The constantly updated database can maximize the practical effects and application value of the monitoring experiment.

II. ACCURATE DETERMINATION OF THE HAIR MERCURY LEVELS

A. Improvement of digestion method

In environmental samples analysis, mercury content is determined in general by cold atomic absorption spectrometry (CAAS) or cold vapour atomic fluorescence (CVAF). In the current environmental monitoring experiment course, the analysis of mercury content in the hair is conducted by digestion of H_2SO_4-$KMnO_4$ and determined by CAAS. However, this method often results in higher blank experimental value and poor accuracy. Therefore, we analyzed the causes from the digesting process and reagent purity.

Generally speaking, under the situation of non-mercury pollution, Hg concentration in hair is quite low (no more than 1 mg/kg) [8]. In order to obtain the accurate testing result of hair Hg contents, it is necessary for the experimental system of CAAS to possess the lower blank value and limit of detection, and the higher accuracy. In the widespread used experimental materials, main reagents such as H_2SO_4 and $KMnO_4$ are analytical reagent, and no purity requirement for other reagents [7]. Reagents itself contains more mercury, likely leading to Hg pollution in experiment. It's worth noting that the reagent $KMnO_4$ can easily oxiding fix more mercury due to its strong oxidizing property, which may result in higher inaccuracy. Accordingly, we made improvement to the digesting method.

Without $KMnO_4$ reagent in digesting process, the mended experiment adopts the acid digestion by mixture of H_2SO_4-HNO_3-V_2O_5 by heating. The purity of reagents is improved, and the guarantee reagent is used as main reagents. Other reagents are at least required purity of analytical reagent. The

experimental reagent purity and specifications are shown in TABLE I.

TABLE I THE PURITY OF MAIN REAGENTS IN IMPROVED EXPERIMENT

Name of reagents	Roles in experiment	Purity
H_2SO_4	Digestion	Guarantee
HNO_3	Digestion	Guarantee
V_2O_5 (Powder)	Catalysis in digestion	Analytical
5% $KMnO_4$ （Purified）	Fixing Hg after digestion	Guarantee
$NH_2OH \cdot HCl$	Reduction of excess $KMnO_4$ before determination	Analytical
$SnCl_2$	Reductant in Hg determination	Analytical

In order to further clarify the effect of the improved experiment, 8 hair samples was used to determine the recovery rate of standard addition and blank value and compare the two digestion methods. The result is listed in TABLE II.

TABLE II COMPARISON OF DIFFERENT DIGESTION METHOD (n=8)

Digestion method	Recovery rate (%)	Blank value (Absorbency)	
		Range	Mean
H_2SO_4-$KMnO_4$	73.8%-132.4%	0.018-0.030	0.023
H_2SO_4-HNO_3-V_2O_5	89.9%-102.6%	0.004-0.011	0.007

The results showed that the recovery rate of H_2SO_4-$KMnO_4$ digestion method is 73.8%-132.4%, and 89.9%-102.6% for H_2SO_4-HNO_3-V_2O_5 digestion method. Apparently, to the accuracy of Hg determination, the improved method is better than the method widely used in current experimental material. A blank value of the method can reflect the influencing degree of experimental instruments, reagents and operation on the response of material to be tested in measurement. Low blank value is the basis of accuracy and reliability of determination. The measuring results showed that the range of blank value is 0.018-0.030, with average 0.023 for H_2SO_4-$KMnO_4$ digestion, and 0.004-0.011, 0.007 for H_2SO_4-HNO_3-V_2O_5 digestion, respectively. The mended method is lower than traditional method extremely significantly by T-test ($P<0.001$). Comprehensive the above results suggest that using high purity reagents and the digestion method of H_2SO_4-HNO_3-V_2O_5 could improve significantly the accuracy of experimental results of determining hair mercury contents.

B. Process management of the experiment

One of the objectives of determining the hair mercury content is reflecting the human Hg exposure in recent time by hair Hg level. In order to obtain accurate and representative results, strict quality control should be used in the whole experimental process, including sampling, washing and determining. The main measures are as follows:

- Hair sampling: if possible, it is better to select the hair on the back side of head due to the good representative according previous study [9]. Therefore, for a long time before experiment, the requirement of hair samples should be sent to college student attending to the test. In addition, the quantity of hair samples can't be too little to ensure good representative.

- Washing samples: the collected hairs should be subject to washing to remove the grease and dirt. Neutral detergent is used in the cleaning process and washed thoroughly with deionized water.

- Drying samples: the washed hair samples are air-dried in the clean filter paper. The protective measures should be taken in the air-dried process to prevent the secondary pollution.

- Breaking samples to pieces: air-dried hair samples are broken to pieces (no more than 0.5 cm) by stainless steel scissors and mixed uniformity.

- Digestion: to make the students master the digesting process, the digestion is divided into different stage with obvious marks such as color variation of digestion solution and gas emitted.

- Detection: in the detection process, standard material is used to ensure the accuracy of Hg determination. Parallel samples and blank test also put into use.

III. CONSTRUCTION OF DATABASE OF HAIR MERCURY CONTENTS FOR COLLEGE STUDENTS

A. Acquisition of data of factors affecting hair Hg contents

There are many approaches causing human health risks of mercury exposure, both internal factors, such as food intake, breathing and drinking, and the external factors, such as hair dye, teeth veneers [10]. Hair mercury content is also affected by other factors, such as living habits and antagonism by other substances. Moreover, there are large individual differences. In order to understand overall the factors affecting the Hg contents and its intensity, a questionnaire is designed for every student attending the test. According previous studies, the main influencing factors in the questionnaire are designed as follows:

- Personal information: age, height, weight, the frequency of hair dye, perm and teeth veneers, etc.

- The seafood habits: frequency of eating fish or shellfish, the part of fish body for eating, producing area of fish products, kinds of seafood, etc.

- Diet and living habits: frequency of eating meat, eggs and milk, dosage of staple food every day, eating habits of vegetables and fruits, frequency of eating garlic, smoking or drinking, etc.

What need points out is that the items in questionnaire could be supplemented according to the new factors found in normal time or other studies.

B. Construction of database hair mercury contents

Accurate determination of the data for the grade of the hair mercury content of college students and individual questionnaire survey is a huge cumulative data resource. Inputting the hair mercury data and corresponding

questionnaire results into EXCEL spreadsheets, the database of college student hair mercury levels is established. Because the student constantly updated and the experiment is conducted every year, the database data can be accumulated and improved. With the database, mercury exposure characteristics of the student groups can be understood and analyzed, and mercury content change tendency could be predicted.

IV. APPLICATION OF HAIR MERCUY CONTENT DATABASE

A. Health risk assessment of mercury for college students

Hair mercury levels can provide the direct exposure status of environmental pollution for the population, which could be used to evaluate the mercury health risks of the student groups. High hair mercury levels may mean high individual risk of health. Furthermore, students are eager to know if they have the mercury health risks after seeing the determination results of the mercury content of themselves. However, there is so far no domestic health risk evaluation criteria system of mercury pollution. Accordingly, we evaluate the health risks with hair mercury levels via a new standard which is recommended by U.S. environmental protection agency (USEPA).

Due to the neurotoxicity of mercury, high mercury pollution can result in paraesthesia of human body. According to the study of USEPA, we grade the hair mercury levels and the corresponding frequency of paresthesia for adults as follows:

- Ⅰ <0.64 mg/kg (Paraesthesia rate<5%)

- II 0.64-1.5 mg/kg (Paraesthesia rate=5%)

- III 1.5-2.8 mg/kg (Paraesthesia rate=25%)

- IV 2.8-5.9 mg/kg (Paraesthesia rate=50%)

- V 5.9-10 mg/kg (Paraesthesia rate=75%)

- VI >10mg/kg (Paraesthesia rate=95%)

In addition, acceptable daily intake (ADI) could be used to assess the mercury health risk. U.S.EPA has made latest ADI of mercury 0.1μg/kg/day, which is corresponding to the hair mercury content 1 mg/kg. When a person's hair total mercury content is more than 1 mg/kg, there will be the health risks of methyl mercury.

B. Using the data for statistical analysis

Constructed database of hair Hg contents and influencing factors for college students is a huge amount of data systems which could be constantly updated. Because related specialized student can experiment every year and data will continue to be added. The data resources can be used in environmental monitoring for integrated training or other related courses. In the environmental statistics course and experiment, the simulated training needs a large amount of data. The data of hair mercury levels and influencing factors can be applied for statistical training. Moreover, due to the hair mercury data coming from the student group, students are effectively attracted, so as to achieve better training effect. The data of hair Hg contents for different groups in gender and eating habits can be used for T test and variance analysis (ANOVA). The

correlation analysis is conducted between hair mercury levels and various influencing factors. The statistical model between hair mercury levels and various influencing factors could be established, so as to forecast the trend of hair mercury levels in the future.

V. TEACHING EFFECT EVALUATION

The reform item of determination of hair mercury content initiated in 2009, and has been implemented in the "environmental monitoring experiment" for more than three years. Years of teaching practice showed that the teaching effect in environmental monitoring experiment is very excellent for students majoring in environmental science. Students collect hair of themselves for the determination of mercury, making follow-up evaluation and statistical analysis, which greatly improves the enthusiasm of attending experiment. The monitoring experiment of hair mercury is changed from a simple determining test to a comprehensive experiment item, integrating sampling, accurate determination, subsequent scientific evaluation and statistical analysis. Comprehensive training effect is greatly increased. Through method improvement and process control of experiment, and subsequent evaluation and statistical analysis, enable students to master how to determine the hair mercury content, how to obtain results with accuracy and representation, and how to evaluate and analyze the test results. It is the methods and principles of scientific research.

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