

Determination of Metal Elements in Workplace Air by ICP-MS

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Abstract. It was important to assess workplace air quality in factory where the air quality has a significant impact on the health of workers. This study aimed to determine the concentrations of metal elements in workplace air of factory. In this article, an easy and quick method based on microwave assisted acid digestion technique prior to quantification using inductively coupled plasma mass spectrometry (ICP-MS) for measuring contents of 7 metal (Cr, Mn, Ni, Cu, Pb, Cd and Sn) elements in workplace air. The air samples were collected by quartz filter membrane. The samples were respectively prepared by microwave digestion system and nitric acid. Under the optimum condition of method, the calibration curves were obtained with correlation coefficients were above 0.9994, the limits of detection of the method were 0.004-0.072 mg/L. The average recoveries of the 7 metal elements at three levels were in the range of 93.8%-102.3%. The proposed method has some advantages of simple operation, high sensitivity and good accuracy.

1 Introduction

Accurate and precise analysis of samples is of crucial importance for clinical, environmental, nutritional, toxicological and forensic sciences [1]. The pollution of metal poisons in the workplace environment is becoming more and more serious [2-5]. In the process of cutting, welding and surface polishing, it is easy to form a large amount of dust. The concentration of heavy metal elements in the dust is higher, and it will cause harm to human body after absorption. At present, the detection methods of metal elements in the air of workplace mainly include volumetric method, flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry, spectrophotometry methods and so on. Volumetry method and spectrophotometry methods are complicated and slow in analysis, flame atomic absorption spectrometry and graphite furnace atomic absorption spectrometry can be used for continuous analysis, but they are more suitable for the determination of single element. Inductively coupled plasma mass spectrometry (ICP-MS) can be used to determine multiple elements at the same time, and has the advantages of low interference level, good precision and wide linear range. In general, the concentrations of metal in workplace air are low. Thus, inductively coupled plasma mass spectrometry, a multi-elemental and highly sensitive analytical technique with wide dynamic ranges, has become the most appropriate technique for the determination of metal in workplace air [6]. Microwave-assisted digestion with acids is a widespread sample treatment method for routine determination of trace elements by ICP-MS in dust

samples [7]. This paper describes a microwave digestion procedure adapted to small sample sizes using volume closed vials for determination of seven elements (Cr, Mn, Ni, Cu, Pb, Cd and Sn) at trace level by ICP-MS. The ICP-MS is widely used for multielement analysis, less reports using ICP-MS for quantitative analysis of metal elements in workplace air. To realize more scientific analysis of workplace air, in this experiment, closed microwave digestion samples were adopted to develop and validate ICP-MS method that enables simultaneous determination of 7 kinds elements in the industrial dusts, in the hope of providing experiment guidance and data reference for metal elements detection.

2 Experimental

2.1 Apparatus

The air samples were collected by Gilian 5000 Personal Air Sampling Pump (SENSIDYNE Industrial Health and Safety Instrumentation). The inductively coupled plasma mass spectrometer (ICP-MS) used was Agilent 7700 ICP-MS mass spectrometer (Agilent Technologies, Inc). A microwave digestion system Multiwave MARS-X microwave digestion system (CEM Company) was used for microwave-assisted digestion of samples. High-purity deionized water obtained from a Millipore ultrapure water system (Millipore, Bedford, MA, USA) was used throughout the work. All lots of the filter paper used in our research sample collection are micro quartz fiber filter paper. All solutions were prepared with 18

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MΩ cm Milli-Q water. The plastic/glass containers were soaked in 10% (v/v) HNO₃ for at least 24 h, and then rinsed extensively with Milli-Q water prior to use. All other reagents used were p.a. grade.

2.2 Reagents and chemicals

The calibration standard solutions were prepared from 10 mg/L multi-element standard solution (GBW08617, China Institute of Metrology). The selected isotopes of the elements for analyses were Bi, Ge, In, Sc and Y, the concentration of the standard solution are all 10 mg/L. Concentration of mass spectrometer tuning solution was 1.0 μg/L. The solution contained beryllium (Be), magnesium (Mg), indium (In), Uranium (U), cerium (Ce) and Barium (Ba) covering the whole spectrum.

2.3 Sample collection site

The sampling sites were set in the factory, and the pollution source and obstacles should be avoided around the sampling site. The height of the breathing band should be selected for the appropriate operation position. Air inlet of sampling pump should not directly aim at the point where dust was generated and directly splashed into the sampling filter membrane. They should be set at the downwind side of the working place.

2.4 Sampling operation

When sampling, the numbered and weighed filter membranes were put into the filter clamp of the clean sampler with the toothless tweezers. The filter membrane hair face should be facing the direction of air inlet, and the filter membrane was firmly pressed. After putting the filter membrane into the sampler, the sampling time and other parameters were set, and air sampling pump was started. After sampling, the filter membrane was taken out with tweezers and put into the filter storage box to record the sampling information.

2.5 Sample analysis

After opening the cover of the filter storage box, the filter storage box was put into the constant temperature and humidity chamber, and the equilibrium temperature and humidity were recorded for 24 hours under the same temperature and humidity conditions before sampling. Under the above equilibrium conditions, the filter membranes were weighed by analytical balance. The same filter membranes were re-balanced under the same conditions in the constant temperature and humidity chamber for 1 h and then weighed. In order to meet the requirement of constant weight, the difference of two weights was less than 0.05 mg, and the arithmetic mean of two weights were taken as the final sample quality.

2.6 Samples preparation and digestion

The samples were collected with quartz filter membrane for 2 hours each time. The air sample volume is 120 L. The samples were stored in an the filter storage box to avoid light. After sent to the laboratory, the samples were analyze as soon as possible.

For micro-wave digestion, sample (cut in small parts (<1.0 mm) was accurately weighed directly into PTFE digestion vessel. Then 9 mL concentrated HNO₃ (70%) and 1.0 mL H₂O₂ was added and digested using microwave system. Sample digestion started in according to conditions set in Table 1.

Table 1. Microwave digestion program

Temperature gradient	Temperature (°C)	Heating-up time (min)	Maintenance time (min)
1	Room temperature	/	/
2	120-150	3	5
3	150-180	3	5
4	180	3	10
5	60	/	30

After completion of the digestion process, the sample solution was cooled in the digestion tank until the temperature sensor indicated that digestion tank temperature was less than 60°C. Then, take out the samples from the microwave digestion system, and then cool in a fume hood. Afterward, open the digestion tank, rinse the cover with ultrapure water, add washing liquid to the digestion vessel, place it on electric hot plate at 120°C for removing acids. When about 5 mL of digestion solution remained, take it down and let it cool. Then transfer digestion solution into a 25 ml volumetric flask, and then wash fume hood with a small amount of ultrapure water repeatedly, before transferred into flask. Then add ultrapure water to volume scale, evenly mix and obtain the sample. On the other hand, prepare sample blank solution.

2.7 ICP-MS condition

By tuning and optimize function of ICP-MS instrument, tuning solution was adopted to tune experiment instruments. Working parameters of the instrument are shown in Table 2.

Table 2. Operation parameters of ICP-MS

Operaiong conditions	Parameters
RF power	1.55 kw
Plasma gas folw rate	15 L/min
Makeup gas flow rate	0.8 L/min
Carrier gas flow rate	0.2 L/min
Sampling depth	10.0 mm
Date points	3 points/peak
Dwell time	100 ms/point
Repetition	3 times
Collision gas	He (5 mL/min)

2.8 Instrument tuning

When the vacuum degree of the instrument reached the requirement, the parameters of the instrument, such as sensitivity, oxide, double charge, quality correction and resolution, were adjusted by the mass spectrum tuner, and the working conditions were optimized. Before samples were tested, ICP-MS needs to be preheated and stabilized for 30 minutes, during which the mass spectrometer tuning solution could be used for quality correction and resolution checking. The relative standard deviation of the signal intensity of the elements in the calibration solution measured was less than 5%. Quality Correction and resolution checks must be carried out for the mass-number range of the elements to be tested.

2.9 Calibration procedure

The external calibration technique was followed for the quantitative analysis of the samples. Standard solutions were made in 5% (w/w) HNO₃ by diluting a multi-element standard solution containing all the analyte elements. The calibration curves for all the analytes were built on same concentrations, from the limit of detection (LOD) of the corresponding element so that concentrations of all analytes in the samples were within linear range of calibration curve. The calibration standards were analyzed at regular intervals during analysis as samples to monitor the instrument drift. Also ultrapure deionised water blanks were frequently analyzed alongside samples to check for any loss or cross contamination. Any slight instrumental drift was taken into account to avoid any possible error. All the

measurements were carried out using the full quantitative analysis mode.

2.10 Quality assurance

The analytical method followed for the determination of metals in workplace air was validated by measuring several quality parameters including sensitivity, linearity, precision, accuracy and spike recovery. Sensitivity of the instrument was estimated through the determination of detection limits of all elements studied. Blank solution was measured 11 times, with its standard deviation calculated and 3 times of the standard deviation was taken as the detection limit. Linearity was established by preparing the calibration curves of all analyte elements using a non-weighted least-squares linear regression analysis method. All calibration curves were prepared with seven standard solutions including the blank. These were prepared in such a way that the concentrations all analyte elements in the samples were within the linear range of calibration curves and above the established lower linearity limit [8]. The analytical quality control for the all metals elements was also verified via recovery experiments by spiking at three selected concentrations of 5 µg/L, 50 µg/L and 100 µg/L.

3 Results and discussion

3.1 Validation of analytical methods

Table 3. Linear regression equations, correlation coefficients, and limits of detection (n=6)

Elements	Linear regression equations	Correlation coefficient	Detection limit (mg/L)
Cr	$y=19113.8x + 2515.3$	0.9996	0.018
Mn	$y=6798.3x + 77.8$	0.9997	0.009
Ni	$y=10374.7x + 2356.1$	0.9994	0.021
Cu	$y=712639.4x + 83196.7$	0.9999	0.072
Pb	$y=58310.7x + 1555.8$	0.9996	0.024
Cd	$y=5110.2x + 1365.8$	0.9997	0.004
Sn	$y=2566.4x + 281.5$	0.9995	0.011

The determination of important quality parameters such as detection limits, linear equations, accuracy and spike recovery experiments proved that the analytical method followed was fulfilling the required criteria for analytical methods specified by Association of Official Analytical Chemists for analysis. Before validation with the

accuracy profile procedure of the 7 elements, we built over a range of concentration levels comprised between the estimated detection limit and the defined highest concentration, it was first necessary to evaluate the linearity and specificity on a range of defined calibration concentrations to estimate the detection limit. The statistical tests were derived from the analysis of variance applied to the least-squares regression.

Table 4. Spike recovery rates of the method (n=6)

Elements	Recovery rate (%)		
	Addition amount at 5 mg/L	Addition amount at 50 mg/L	Addition amount at 100 mg/L
Cr	95.3 ± 3.0	98.9 ± 0.5	99.4 ± 0.4
Mn	96.2 ± 5.5	97.2 ± 0.4	99.2 ± 0.1
Ni	93.8 ± 4.2	96.4 ± 0.8	98.8 ± 0.2
Cu	98.8 ± 3.7	99.2 ± 1.1	102.3 ± 1.4
Pb	101.4 ± 2.5	98.8 ± 0.4	98.6 ± 0.5
Cd	96.5 ± 3.8	96.2 ± 1.5	99.2 ± 0.3
Sn	97.3 ± 4.2	95.7 ± 0.8	98.0 ± 0.5

As shown in Table 3, the 7 elements show a good linear relationship in the concentration range within 0-1,000 mg/L. Blank solution was measured 6 times, with its standard deviation calculated and 3 times of the standard deviation was taken as the detection limit. The detection limit of this method was 0.004-0.072 mg/L. The statistical tests results indicated that the linear regression model was considered acceptable for measuring the contents of the 7 elements and the linearity rang was validated from 0 to 1,000 mg/L for Cr, Mn, Ni, Cu, Pb, Cd and Sn. Table 4 shows that standard recovery rate of 7 elements in workplace air is between 93.8% and 102.3%. These good recoveries further confirmed that there was no significant loss or gain for each analyte during the digestion procedure. Based on these results for the quality parameters analyzed, the analytical method followed in this research study was found quite efficient to determine the contents of all metals elements in workplace air.

3.2 Standard sample determination

Under the optimized conditions, according to the preparation method of sample solution, the content of each standard sample was determined. As shown in Table 5, the results showed that the measured values

were in the range value of uncertainty. It shows that this method could be used for the detection and analysis of actual samples.

Table 5. Determination of metal elements in filter membrane standard sample (n=3)

Metal element	Standard (µg/paper)	Uncertainty	Measured (µg/paper)
Cr	30	1.8	29.3
Mn	20	4.0	20.3
Ni	42.2	1.5	41.9
Cu	20	1.2	19.6
Pb	3.2	0.8	3.1
Cd	30	1.8	19.2
Sn	12	2	11.8

3.3 Reagent blank test

Each batch samples, which need to 3 blank sample, using pure water and nitric acid reagent used in the laboratory, did not add the filter membrane. Samples were prepared with the sample pre-treatment operation to determine on the machine after treatment. The blank sample value was less than the Limit of quantitation (MDL). When the blank sample value was more than 2.2 times over the MDL, the reason must be found out, and the sample must be reprepared and determined after the pollution source was eliminated.

3.4 Samples blank test

Each batch samples need to 3 blank samples for the quality control. The samp collection equipment including the blank filter membrane, tweezers and so on was brought to the scene, was prepared with the sample pre-treatment operation. The blank value was required to be less than the method quantitative limit.

3.5 Sample determination

When the concentration of an element exceeded the linear range of the working curve, the sample should be properly diluted and re-analyzed, and re-taken double parallel sample analysis.

3.6 Sample analysis results

According to the working parameters of selected instruments and related methods and conditions, the 7 elements contained in the 54 samples which have had gone through microwave digestion were measured by ICP-MS method, and measurement results are shown in Table 6. When the air sample volume is 120 m³, their concentrations were found to be variable among the different places. As shown in Table 4, concentrations of metals were ranged for Cr (5.7×10^{-4} - 3.9×10^{-3} mg/m³), Mn (4.3×10^{-4} - 8.3×10^{-1} mg/m³), Ni (8.6×10^{-5} - 5.8×10^{-3} mg/m³), Cu (5.6×10^{-4} - 5.7×10^{-1} mg/m³), Cd (3.2×10^{-5} - 2.7×10^{-3} mg/m³), Sn (4.8×10^{-4} - 2.6×10^{-2} mg/m³) and Pb (5.1×10^{-5} - 2.6×10^{-2} mg/m³). It can be seen from the Table 4 that the contents of 7 metals in the air sample are non-normal distribution, the content of Mn and Cu is the highest, the content of the other 5 metals are very low. There is a high risk of Mn exceeding the legal limit in the workplace air.

Table 6. Determination results of metallic elements in workplace air

elements	quantity (n)	extreme value (mg/m ³)	Median value (mg/m ³)	^a eference standard (mg/m ³)
Cr	54	5.7×10^{-4} - 3.9×10^{-3}	1.2×10^{-3}	0.05
Mn	54	4.3×10^{-4} - 8.3×10^{-1}	2.1×10^{-3}	0.15
Ni	54	8.6×10^{-5} - 5.8×10^{-3}	5.4×10^{-4}	1.0
Cu	54	5.6×10^{-4} - 5.7×10^{-1}	6.2×10^{-3}	1.0
Cd	54	3.2×10^{-5} - 2.7×10^{-3}	8.4×10^{-4}	0.01
Sn	54	4.8×10^{-4} - 2.6×10^{-2}	5.4×10^{-3}	2.0
Pb	54	5.1×10^{-5} - 2.6×10^{-2}	5.9×10^{-4}	0.05

^a Indicates that occupational exposure limits is the allowable concentration for short-term contact (PC-STEL)

4 Conclusions

This paper studied a new method for simultaneous analysis and detection of 7 metal elements in workplace air with microwave digestion inductively coupled plasma mass spectrometry. The method features rapid analysis speed and wide linear range. After one-time sample digestion, 7 elements in workplace air can be determined simultaneously with high accuracy and sensitivity. Under the optimum condition of method, Linearity was established by preparing the calibration curves of all analyte elements using a non-weighted least-squares linear regression analysis method. The calibration curves were obtained with correlation coefficients were above 0.9994. The limits of detection were calculated with three the standard deviation of the blank divided by the

slope of the analytical curve respectively. The limits of detection of the method were 0.004-0.072 mg/L. The average recoveries of the 7 metal elements at three levels were in the range of 93.8%-102.3%. The 7 metal elements in workplace air of factory had been accurate measured by ICP-MS method. The results showed that microwave digestion-inductively coupled plasmamass spectrometry can quickly and simultaneously determine Cr, Mn, Ni, Cu, Pb, Cd and Sn elements in workplace air.

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