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Detection of heavy metals in aqueous solution using PGNAA technique

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Abstract A prompt gamma neutron activation analysis setup was developed for heavy metal detection in aqueous solutions with a 300 mCi ^{241}Am-Be neutron source and a 4 × 4 inch (diameter × height) BGO detector. In the present work, heavy metals, including Mn, Cu, Ni, Cr and Zn, were measured by the setup. The minimum detectable concentrations of Mn, Cu, Ni, Cr and Zn were 246.6, 391.2, 218.1, 301.5 and 2804.1 ppm, respectively. The minimum detectable concentration of each element and the linearity response between the characteristic peak counts and elements concentrations have been studied. And the results showed that all heavy metals had a good linear relationship between characteristic peak counts and concentrations.

Keywords Prompt gamma neutron activation analysis · Heavy metals · Linearity response · Minimum detectable concentrations

1 Introduction

Nowadays, more and more people realized that environmental pollution, especially the distribution and diffusion of heavy metal pollution in the soil and water, brings a high risk to the local environment and citizens. Therefore, the development of methods for measuring heavy metals is appreciated. The conventional methods, including chemical analysis, spectrophotometric method, atomic absorption spectrophotometry and other, are very time-consuming and expensive [1], and the samples need to be collected and prepared before analyzing. To tackle these problems, PGNAA can be considered as a suitable technique for an in situ, rapid and continuous survey of such heavy metal pollutants [2].

PGNAA is a powerful nuclear analytical technique for the determination of elements. It has been applied in many fields, including on-line and in situ measurements, and environmental and nondestructive analysis [3–8]. The method is mainly based on some of the most basic nuclear reactions, thermal neutron capture and neutron inelastic scattering reactions. The number of prompt gamma rays, which are emitted from the sample during the reactions, is proportional to the amount of elements.

To discuss the possibility of heavy metal detection in aqueous solutions using the PGNAA technique, some works have been studied by some organizations. A detection facility containing a 0.125 m^3 volume of water, ^{241}Am-Be neutron source, and high-purity germanium gamma-ray detector was designed by Khelifi et al., and some heavy metals, such as Mn, Cu, Ni and Cr, were studied by the setup [9]. Naqvi et al. used a moderator to get the thermal neutrons from the neutron generator and then detected the samples containing Cd and Hg [10, 11]. In our previous work, a PGNAA setup for element detection of aqueous samples has been designed [12].

In this paper, heavy metals, including Mn, Cu, Ni, Cr and Zn, were detected with the PGNAA setup, which was designed in our earlier work. The linearity response between

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the characteristic peak counts and concentrations of heavy metals was studied. The minimum detectable concentration of each element was also discussed.

2 Experimental

2.1 PGNAA setup

A schematic diagram of the setup is shown as Fig. 1. The setup consists of a 300 mCi ^{241}Am-Be neutron source and a cylindrical 4 × 4 inch (diameter × height) BGO detector (Saint-Gobain, the energy resolution is 9.7 % for 662 keV gamma rays from the ^{137}Cs source). The neutron source is placed at the center of the setup. The BGO detector is located at the external surface of the polymethyl methacrylate tank and parallel to the vertical centerline. The detector is connected to an ORTEC model digibase

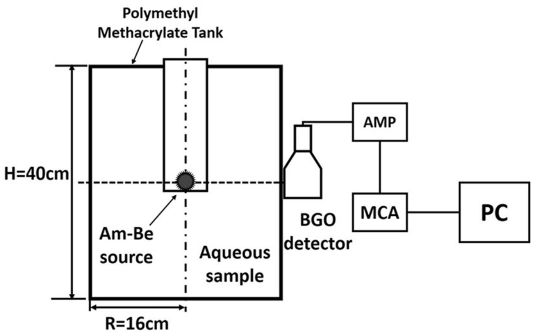

Fig. 1 Schematic diagram of PGNAA setup

Table 1 Prompt gamma rays and microscopic absorption cross-section of the heavy metals

Element	E_γ (MeV)	σ_s (barns)
Mn	7.270	0.362
	7.243	1.36
	7.159	0.643
	7.057	1.22
	5.527	0.788
	5.014	0.737
Cu	7.915	0.869
Ni	8.998	1.49
	8.533	0.721
Zn	7.863	0.141
Cr	8.884	0.78
	8.51	0.233
	8.482	0.169
	7.938	0.424

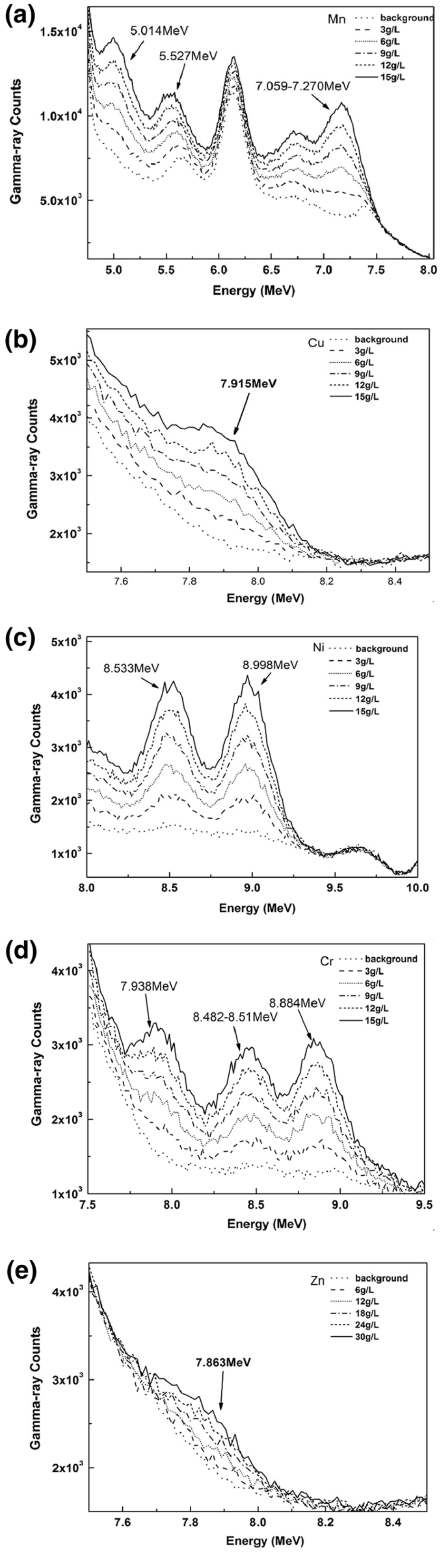

Fig. 2 The prompt gamma-ray spectra of heavy metals (**a** Mn, **b** Cu, **c** Ni, **d** Cr, **e** Zn)

multi-channel analyzer. The radius and height of the tank were set to 16 cm and 40 cm according to Monte Carlo optimization, respectively [12]. The aqueous samples, which play a very important role in moderating neutrons, are in the cavity separated from the source by a tube. The energy calibration of the setup is performed using the characteristic gamma rays emitted from the ^{60}Co, ^{137}Cs, ^{241}Am-Be neutron source, and prompt gamma rays by hydrogen neutron capture.

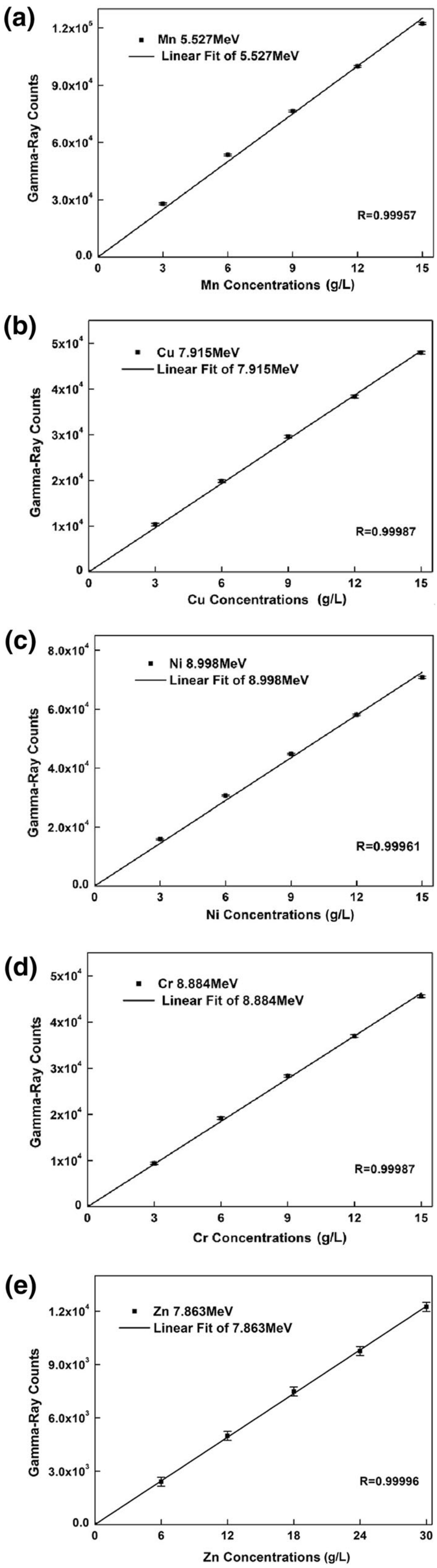

Fig. 3 The gamma-ray counts vs. concentrations of heavy metals (**a** Mn, **b** Cu, **c** Ni, **d** Cr, **e** Zn)

2.2 Sample preparation and data acquisition

Aqueous solution samples containing Mn, Cu, Ni, Zn and Cr were prepared by dissolving their respective compounds in deionized water. The prompt gamma-ray energies and microscopic absorption cross-sections of these metals are listed in Table 1 [13]. For all the elements above, five samples with different concentrations were prepared. The concentrations of Mn, Cu, Ni and Cr were 3, 6, 9, 12, 15 g/L. The concentrations of Zn were 6, 12, 18, 24, 30 g/L due to its small neutron capture cross-section. The deionized water was considered a background.

The samples and background were measured by the setup, mentioned above, at the Institute of Nuclear Analysis Techniques, located at Nanjing University of Aeronautics and Astronautics. The pulse pile-up and dead-time were considered in the measurement. Since modern spectrometers have accurate live-time clocks, these corrections are achieved by using live-time. The measurement time was then set to 3600 s with live-time, and the spectrum was acquired by the software GAMMAVISION.

3 Results and discussion

Figure 2a–e shows the gamma-ray spectra of the BGO detector from the aqueous samples contained in heavy metals. For each element, there were five samples containing different concentrations. The deionized water was

Table 2 The MDC of the heavy metals in the water with the setup

Element	E_γ (MeV)	*MDC* (mg/L)
Mn	5.527	246.6
Cu	7.915	391.2
Ni	8.998	218.1
Cr	8.884	301.5
Zn	7.863	2804.1
Hg [12]	5.967	51.4
Cd [15]	0.558	7.0

Table 3 The MDC of heavy metals in the water using other setups

Setup	Neutron source	Activation (Ci)	Measuring time (s)	*MDC*						
				Mn	Cu	Ni	Cr	Zn	Hg	Cd
Ref. [4]	^{241}Am-Be	1	14,000	870	900	/	620	7600	87	6.7
Ref. [9]	^{241}Am-Be	1	7200	150	189	99	271	7990	23.8	2.7

considered a background. It can be seen that the spectra of prompt gamma rays of the heavy metals contained different concentrations superimposed upon each other, along with the background spectrum. The characteristic gamma rays of Mn, Ni and Cr can be seen directly, while Cu and Zn are not so clear due to the small absorption cross-section in the spectra. Next, the background spectrum was subtracted from the samples spectra. And the peaks of difference spectra were found and integrated to generate measured counts of prompt gamma-ray peaks of heavy metals [11].

The measured counts of the chosen gamma rays from Mn, Cu, Ni, Cr and Zn plotted against their respective concentrations are shown in Fig. 3a–e. It can be seen from the figures that the count varies linearly with the amount of each element. All coefficients of correlation of the linear fit are greater than 0.999. The absorption cross-sections of these heavy metals are small, so that the effect of neutron self-shielding can be ignored. Hence, the results show a good linear relationship between the counts of prompt peak with their concentrations. In our previous work, Cl, B, Hg and Cd were studied with the setup [12, 15]. However, the coefficients of correlation of the linear fit of these elements are poorer than those of the heavy metals due to their large neutron absorption cross-section. Neutron self-shielding has a significant influence on the elements' measurement. Some methods have been used to correct the effect of the neutron self-shielding [14].

In order to describe the detection limits of the elements measured by this setup, the minimum detectable concentrations (*MDC*) of the setup for these elements are calculated. The *MDC* and the errors are calculated by the following Eq. [16]:

$$MDC = 4.653 \times \frac{C}{P} \times \sqrt{B} = 4.653 \times \frac{C}{p} \times \sqrt{\frac{b}{t}}, \tag{1}$$

$$\sigma_{\mathrm{MDC}} = \frac{C}{P} \times \sqrt{2 \times B} = \frac{C}{p} \times \sqrt{\frac{2 \times b}{t}}, \tag{2}$$

where C is the concentration of the element of interest; P and B are the net count and background count of the characteristic peak, respectively; p and b are the net count and background count rate of the characteristic peak, respectively; t is the measured time.

The *MDC* of the heavy metals at the chosen characteristic energies are determined by the PGNAA setup with a time of 3600 s. The results are listed in Table 2. It can be seen that only cadmium could be obtained with the detection limit in the order of ppm, while mercury can be determined in the order of 100 ppm. The *MDC* of Mn, Cu, Ni and Cr are all in the range of 200–400 ppm. However, the detection limit of Zn is in the order of mg/mL due to its small absorption cross-section. To improve the detection limits of heavy metals, using a more intense neutron source or taking a longer time measurement can be considered. Both the improvements can make this facility a more powerful tool in analyzing heavy metal pollutants.

References [4] and [9] reported some minimum detection limits for heavy metals. The results are listed in Table 3. Compared to these works, the setup we designed performs well in heavy metal detection.

4 Conclusion

A PGNAA setup with a ^{241}Am-Be neutron source and BGO detector has been used to detect heavy metals in water. The results show that the facility can be used for the determination of some heavy metal pollutants. The detection limits for heavy metals, which are commonly found in polluted water, were evaluated and predicted to investigate the potential application of the probe for in situ measurements. Higher detection sensitivity can be obtained by increasing neutron flux or taking a longer time measurement.

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