

## APPLICATION OF XRF TO MONITORING HEAVY METALS IN SOILS AND SEDIMENTS

Shangjun Zhuo, Ang Ji

Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

Ore mining and industrialization bring rapid growth in GDP as well as serious pollution for developing countries. Heavy metals pollution is one of the environmental problems of particular concern to Chinese government. It was estimated that China has the largest number of tailing dams in the world. Both tailing dams and mining drainage are dangerous sources of heavy metals pollutions. Industrial waste gas emission, industrial waste water discharge and industrial dusts diffuse hazardous heavy metals through water and wind. Those kinds of pollution may lead to higher levels of heavy metals than normal in soils, water and water sediments. Food crops planted in the polluted soil and/or irrigated by the polluted water may have higher levels of heavy metals than normal. The concentration of Cd in rice, for instance, gets higher if the planted land and the irrigating water are rich in Cd.

More and more strict laws are making to prevent those kinds of pollution. China implemented environmental standard for soils in 1995 and technical regulations for environmental monitoring for soils used to plant food crops in 2004. In those regulations, most of the trace elements are determined by solution based specimen methods, such as AAS, ICP-OES and ICP-MS etc. X-ray fluorescence spectrometry (XRF) has the advantage that it can measure the solid specimen with very simple sample preparation. However the sub-ppm level of detection limits requirements for the trace elements make it difficult for traditional XRF methods to meet them.

A wavelength dispersive XRF spectrometer with high power (Panalytical Axios advance, Rh target, 60kV, 4kW) coupled with a high energy polarized energy dispersive XRF spectrometer (Panalytical Epsilon 5, Sc-W target, 100kV, 0.6kW) have been successfully used to determine more than 50 trace elements in soils and water sediments. Nakai's review of the high energy XRF and its applications showed ppm level detection limits for heavy elements (High-energy X-ray Fluorescence, X-ray Spectrometry: Recent technological advances, edited by K. Tsuji, J. Injuk and R. Van Grieken, John Wiley & Sons, Ltd, 2004, 355-372). By optimizing the operating conditions, in our case, the detection limits for most of the elements can be lowered to sub-ppm level and meet the requirements of the technical regulations for environmental monitoring for soils (see Table 1).

Table 1 Detection limits (DL) for some trace elements in soils required for the technical regulations for environmental monitoring and the measured values (300s)

Element	Required DL(ppm)	Measured DL(ppm)	Element	Required DL(ppm)	Measured DL(ppm)	Element	Required DL(ppm)	Measured DL(ppm)
Cr	6.0	5.0	Se	0.30	0.20	Pb	1.0	0.60
Mn	6.0	3.0	Mo	0.20	0.10	Bi	0.30	0.10
Co	0.56	0.50	Cd	0.20	0.20	Th	1.0	1.0
Ni	1.0	1.0	Sn	0.50	0.50	U	1.0	0.50
Cu	1.0	0.5	Sb	0.40	0.35	15 Rare earth	0.50/1.0	0.2~1.0
Zn	1.0	1.0	Hg	0.10	0.10			
As	0.20	0.20	Tl	0.50	0.20			

The optimized operating conditions include: setting the right exciting power, selecting the right secondary exciting targets, using the right filters, and employing the right spectrum fitting procedures for high energy polarized energy dispersive XRF spectrometer. As an example, The element Cd in the China national soil reference material GBW 07405 was measured with different secondary targets and secondary target-filter combinations. The certified value for Cd is  $(0.45 \pm 0.09)$  ppm. If CsI and CeO<sub>2</sub> secondary targets are used, Compton scattering from I and Ce K $\alpha$  lines overlap Cd K $\alpha$  line makes it hard to quantify the Cd content. A Zr filter can be used to reduce the background from the Compton scattering. When CsI secondary target-Zr filter combination was used, the error of the measured Cd value was 0.59 ppm, and the error reduced to 0.26 ppm if the Compton scattering peak was used as internal ratio. The sample preparation is simple. For speed measurements, soil or sediment samples can be loaded directly in liquid sample cups with 3  $\mu$  m or 6  $\mu$  m Mylar film. Otherwise the samples can be dried and pressed to disks for measurements to improve the repeatability and accuracy.

It can be concluded that XRF is a qualified method for monitoring the heavy metals in soils and sediments if correct operating conditions are used.