



LAB REPORT XRF 423

S2 PICOFOX Analysis of Heavy Metals in Sewage Samples

Introduction

In general there are many strict international decrees with regard to the discharge of sewage. In Table 1 the valid threshold values for the concentration of toxic heavy metals in sewage in Germany are listed.

The suitability of the TXRF spectrometer S2 PICOFOX for the analysis of sewage samples in the original, highly muddy state and as an aqua regia digestion (ARD) is described in this paper.

A matrix-adapted artificial control solution was used for an assessment of accuracies.

Table 1: Threshold values for heavy metals in sewages*

Element	Threshold value
Arsenic	0.1 mg/l
Lead	0.5 mg/l
Cadmium	0.1 mg/l
Chromium (total)	2.0 mg/l
Cobalt	0.5 mg/l
Copper	1.0 mg/l
Molybdenum	1.0 mg/l
Nickel	2.0 mg/l
Zinc	2.0 mg/l

*: Gewässerschutzverordnung, SR 814 201, Anhang 3.2., 18.12.2001

Table 2: Technical parameters of the TXRF spectrometer S2 PICOFOX

Tube	Air-cooled metal ceramic Mo-anode Max. power 50 W
Optics	Multilayer Monochromator (17.5 keV)
Detector	Si drift detector XFlash® Area: 10 mm ² FWHM: < 160 eV (Mn K α)
Size (DxWxH)	450 x 590 x 300 mm
Weight	37 kg

Table 3: Calculated lower limits of detection (3 σ , 1000 seconds), results in (mg/l)

	Control solution	Sewage (ARD)	Raw sewage
P	0.237	0.292	0.499
S	0.182	0.224	0.382
Cl		0.149	0.255
K	0.068	0.084	0.144
Ca	0.054	0.067	0.114
Ti		0.036	0.059
Cr	0.019	0.023	0.040
Mn	0.014	0.018	0.030
Fe	0.011	0.014	0.024
Co	0.010	0.012	0.020
Ni	0.008	0.01	0.017
Cu	0.007	0.009	0.015
Zn	0.006	0.007	0.013
Se	0.005		0.010
Sr	0.006		0.010
Ba	0.048	0.059	0.137
Hg		0.009	0.015
Tl	0.007		
Pb	0.007	0.009	0.015
Bi	0,007		

Analysis

The most important technical parameters of the TXRF spectrometer are summarized in Table 2.

Because of the highly concentrated matrix, the samples were diluted 1:1 with H₂O^{suprapur}. Gallium was used as an internal standard.

5 μ l of each sample solution were pipetted onto a quartz glass disc and dried in a dessicator. The measurement time was 1000 seconds with a tube setting of 50 kV/1000 μ A.

Results – Lower limits of detection

The calculated lower limits of detection (LLDs) are distinctly below 1 mg/l (Table 3). The element molybdenum cannot be analyzed due to the use of an X-Ray tube with a Mo-anode in the S2 PICOFOX.

The same applies to cadmium, which can only be detected by its L-lines. The concentration in the samples analysed here result in L-line intensities far too low for Cd detection.

The lower limits of detection for all other heavy elements are significantly below the threshold values. The values for the also important element mercury are not reliable because it is volatile during the preparation steps. This problem occurs with classical ICP-OES analysis too.

Results - accuracies

Comparing the measurements results with those obtained by ICP-OES analysis, it is obvious that the analytical data for the digested sample are in good correspondence (Fig. 1b).

The results for the raw sewage sample show distinct deviation from those of the ICP-OES analyses (Fig. 1a). The reason for this deviation is most presumably the sample inhomogeneity caused by the present sludge particles. Furthermore, a direct comparison of the total raw sewage and the filtered aqua regia digestion is severely limited. With regard to the analysis of the control solution, a good correspondence with the nominal values can be observed (Fig. 1c).

The TXRF results for raw and digested sewage (Fig. 2) show also good conformity. The deviation of the marked elements is the result of the volatility during sample preparation (Cl, Br and Hg) or the absorption by sludge particles (Ti).



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