



TXRF

Analysis of Heavy Metals in Sewage Samples

Application Note # XRF 423

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.

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

Table 1

Threshold values for heavy metals in sewages (Gewässerschutzverordnung, SR 814 201, Anhang 3.2., 18.12.2001)



Figure 1
Sewage

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 µl 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 µA.

Results – Limits of detection

The calculated limits of detection (LODs) 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 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.

Parameter	Specifications
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 Kα)
Size (DxWxH)	450 x 590 x 300 mm
Weight	37 kg

Table 2

Technical parameters of the TXRF spectrometer S2 PICOFOX

Element	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	0.010	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		

Table 3

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

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 (Figure 1b).

The results for the raw sewage sample show distinct deviation from those of the ICP-OES analyses (Figure 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 (Figure 1c).

The TXRF results for raw and digested sewage (Figure 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).

Conclusion

The following conclusions can be drawn from the measurement results:

- The heavy metals Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Ba and Pb can be analysed in sewage with the TXRF spectrometer S2 PICOFOX. The S2 PICOFOX allows fast monitoring of threshold values of the respective environmental terms.
- Due to restrictions of the S2 PICOFOX, the elements Cd, Mo, Ag, Sn and Sb cannot be determined in the present concentration ranges and matrices.
- The quantitative detection of the volatile Hg is not possible by either TXRF or ICP-OES.

The advantage of TXRF is the fast and direct measurement of a wide range of elements without any pretreatment of the sewage.

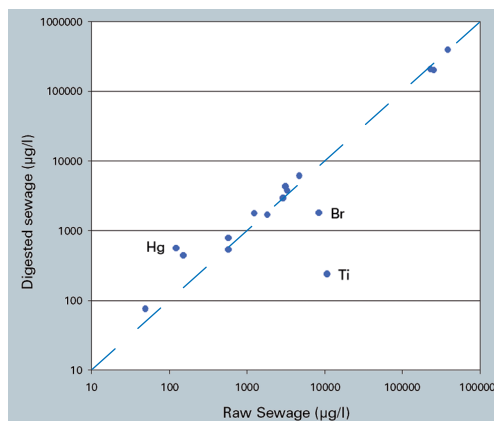
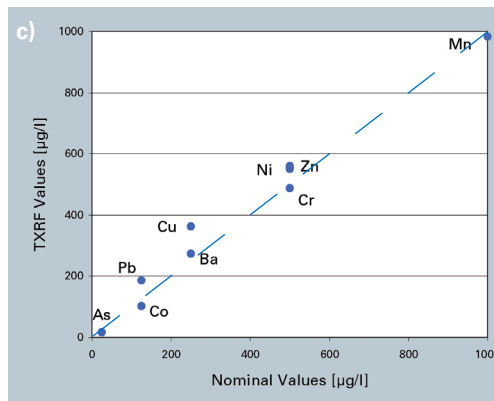
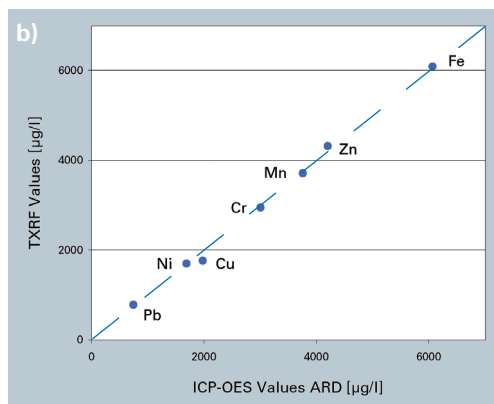
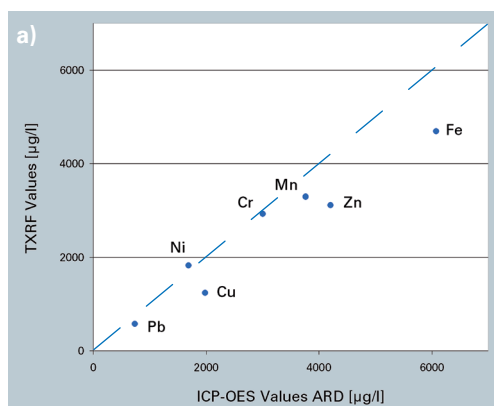


Figure 1

Comparison of S2 PICOFOX measurement results with rated values from ICP-OES analysis and the control solution for the samples raw sewage (a), sewage after aqua regia digestion (ARD) (b) and control solution (c).

Figure 2

Comparison of the S2 PICOFOX measurement results for raw sewage and sewage after aqua regia digestion.

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