TXRF

Rapid and cost-effective monitoring of sludge and wastewater by TXRF spectroscopy

Application Note # XRF 458

Introduction

International standards define analytical methods for the determination of dissolved and particulate bound elements in water (e.g. ground, surface, fresh, drinking and wastewater) [1]. Although, total reflection X-ray fluorescence analysis (TXRF) is not approved yet for wastewater monitoring.

Procedures for the quantitative analysis of Hg or As, Cd, Cr, Ni, Pb, and other elements in wastewater were described recently and their results were compared with ICP-OES/MS data [2, 3]. This lab report demonstrates the use of TXRF spectroscopy for trace element analysis of synthetic wastewater samples and sludges from industrial processes. A special focus is set on the analysis of thallium (Tl), which typically fails when using ICP-OES.

Figure 1
Outflow pipe for wastewater containing sludge – a nightmare for analytical chemists

Part I: Wastewater samples

The performance of TXRF spectroscopy for wastewater analysis was proven by the analysis of several different types of synthetic wastewater containing approximately 0.5 mg/l of a range of elements.

Sample preparation

Seven different synthetic wastewater samples were prepared for TXRF analysis. To achieve a thin and homogeneous sample layer on the quartz sample carrier, 100 µl Polyvinyl alcohol solution (0.3 g/l) were added to 1 ml sample. 10 µl of a Gallium standard solution (0.1 g/l) were added for internal standardization.

After thorough homogenization 10 µl sample were pipetted on a siliconized quartz glass sample carrier and vacuum-dried for about 10 min.

All samples were prepared ten times and measured in the S2 PICOFOX TXRF spectrometer with Mo excitation (50 kV, 600 µA) for 1000 s.

Detection limits were calculated according to the equation:

$$LOD_i = 3 \cdot \frac{3 \cdot C_i \cdot \sqrt{N_{BG}}}{N_i}$$

LOD_i: limit of detection of the element i
C_i: concentration of the element i
N_i: area of the fluorescence peak in counts
N_{BG}: background area subjacent the fluorescence peak

The method detection limits were calculated according to the US Environmental Protection Agency (EPA) method for calculation of MDL, 40 CFR Part 136, APPENDIX B, revision 1.11

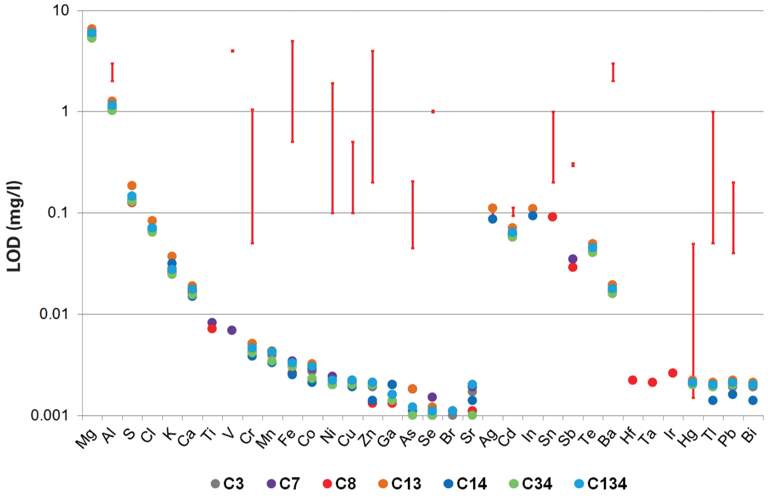

Figure 2

Detection limits for TXRF measurements of seven different synthetic wastewater samples (colored dots). The red bars indicate the legal limits for different German industries.

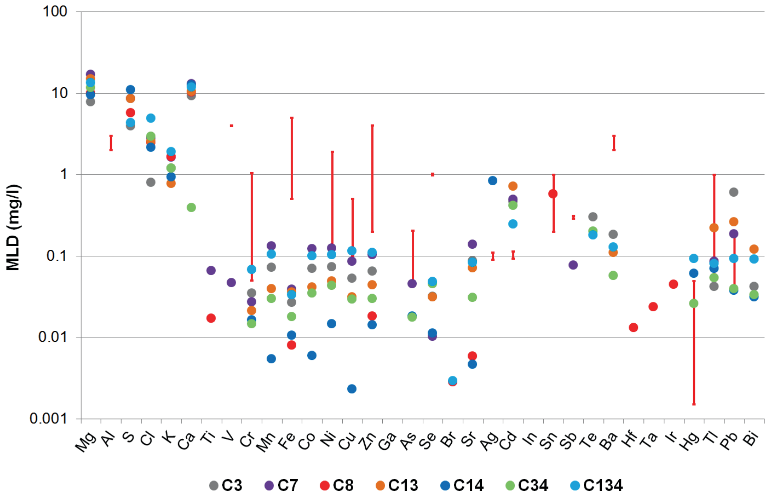

Figure 3

Method detection limits for TXRF measurements of seven different synthetic wastewater samples (colored dots) according to the US-EPA. The red bars indicate the legal limits for different German industries.

Results

Maximum contaminant levels (MCL) in wastewater vary strongly depending on countries and industries. The legal limits of detection for a number of different German industries are shown as red bars in Figures 2 and 3. As an example the MCL for Ni and Cr in the production of ceramics is set to 0.1 mg/l and in the steel industry to 0.5 mg/l. In the print industry Ni values of 2 mg/l and Cr values of 1 mg/l are acceptable.

As shown in Figure 2 for a wide range of elements (Ti, Va, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Hf, Ta, Ir, and Bi) TXRF provides detection limits below 10 µg/l with full recovery rates ± 10% (see Figure 4).

Considering an acceptable range of the US-EPA of 30% (blue area in Figure 4), also elements like Ba, Tl, and Pb can be quantified accurately. The detection limits for Tl and Pb are typically in the range of 2 µg/l in synthetic wastewater. Detection limits below 4 µg/l can be achieved for Hg after fixation by a treatment with thiourea (details not shown). W was only present in one sample (LOD: 2 µg/l), though details are not shown here.

These results clearly demonstrate that the detection limits achieved by TXRF measurements are far below the legal limits for wastewater in most countries. Therefore, TXRF is a suitable technology for the rapid analysis of all considered elements.

Even in case of the more strict method detection limits by the US-EPA most elements can be detected and quantified at concentration levels far below these limits (Figure 3).

TXRF also measures the elements Ag, Cd, In, Sn, Sb, and Te in the concentration range of the legal limits. This allows a quick examination of any wastewater sample. In case of a positive indication an enrichment procedure as described in recent papers [2, 3] has to be applied for a more sensitive and accurate quantification.

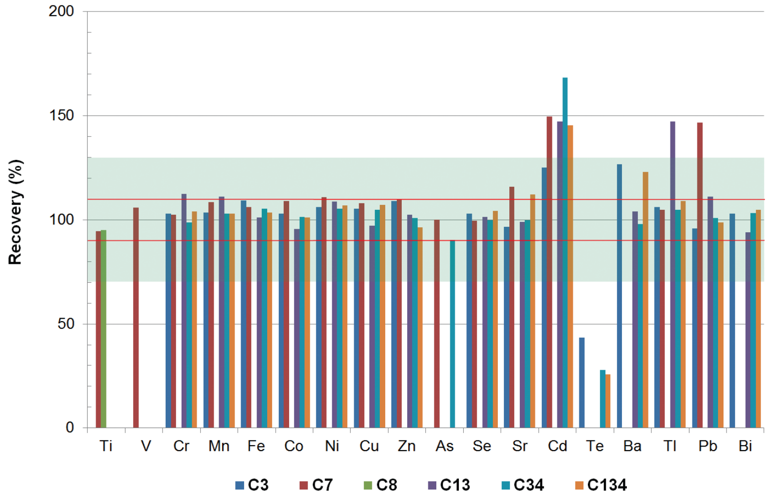

Figure 4

Recovery rates of TXRF measurements for specific elements. The red lines show a deviation range of ± 10%, the grey area shows a range of ± 30% according to the US-EPA.

Conclusion

This paper describes the successful application of TXRF measurements for the multi-element analysis of wastewater. Most elements can be directly quantified after a short and easy sample preparation procedure without any digestion or treatment with hazardous chemicals. Typical detection limits are far below most legal limits.

For a few elements the detection limits are close to the legal limits, but a screening for a quick check against defined threshold levels is still possible.

Part II: Special topic Tl analysis

About ten tons of thallium (Tl) are produced per year, mainly in China, Kazakhstan and Russia. There is a possibility of Tl being discharged into surface water through waste combustion. Tl is toxic with a lethal dose of about 10 mg/kg body weight. Therefore, the German wastewater ordinance defined a maximum permissible value typically in the range of 50 µg/l. Today, Tl is typically measured by AAS or ICPOES, but in practice data are often unreliable.

TXRF was applied for the measurement of five wastewater samples with a high matrix content of almost 1%. Optimal reproducibility of TXRF measurements was achieved after a 1:3 dilution with 0.5 mol nitric acid, the use of Pt as internal standard, sample drying on quartz carriers at 40°C and a measurement time of 2000 s. The TXRF results were compared with ICP-MS and ICP-OES data.

Results

The Tl concentrations in all wastewater samples were typically below 100 µg/l. In wastewater with high matrix content the limit of detection was calculated to be 29 µg/l. The LOD for samples with low matrix content was better than 4 µg/l. As shown in Figure 5 the TXRF values were in good concordance with ICP-MS results and also different AAS measurements (not shown). Interestingly, the ICP-OES measurements from two independent laboratories failed, the recovery rates were generally between 40% and 70% only.

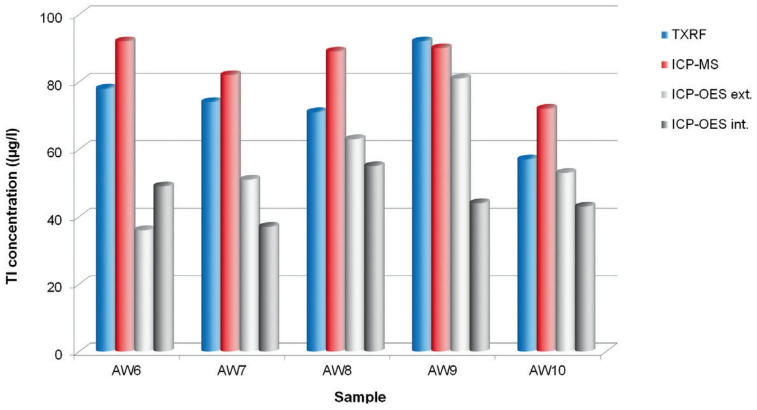

Figure 5

Round robin test for determination of Tl concentrations in different wastewater samples

Conclusion

In contrast to ICP-OES, TXRF is a reliable analytical technology for the detection of Tl traces in wastewaters. The limits of detection are significantly below most legal limits. The total process time including sample preparation and calibration for any AAS or ICP measurement of Tl typically exceeds 1 hour. Although TXRF measurement times are quite long (>10 min), the total process time is in the range of 20 to 40 min and therefore significantly shorter.

Acknowledgement

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References

[1] DIN EN ISO 11885:2009-09

[2] Marguí, E., Tapias, J.C., Casas, A., Hidalgo, M., Queralt, I., Chemosphere 2010, 80 (3), 263-270

[3] Marguí et al., Talanta 2010, 82 (2), 821-827

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