TXRF

Tungsten (W) Excitation and its Application to Pharmaceutical and Environmental Samples

Application Note # XRF 436

Introduction

The S2 PICOFOX working principle is based on the method of total reflection X-ray fluorescence (TXRF) analysis. Typically an air-cooled X-ray tube with molybdenum target in combination with a multilayer monochromator and a cut off at 17.5 keV is used as excitation source. For elements up to Z = 39 (Y) detection limits down to the sub-ppb range or 1 pg absolute mass can be achieved due to the extremely low background of the Mo excitation.

Heavier elements have to be detected by the L-lines, which also leads to detection limits in the low ppb range for the element range from cesium to uranium (Z = 55 - 92). Due to the presence of potassium, calcium and other light elements in most matrices and argon in the air, the detection of L-lines from zirconium to iodine (Z = 40 - 53) is limited. Various application areas require the accurate detection of those elements, e.g. palladium as catalyst in pharmaceutical production (see Figure 3) or cadmium and antimony as toxic key elements for environmental protection.

In this report the application of the tungsten excitation for detection of trace amounts of palladium in pharmaceutical and cadmium in environmental samples is described.

Figure 1

Palladium

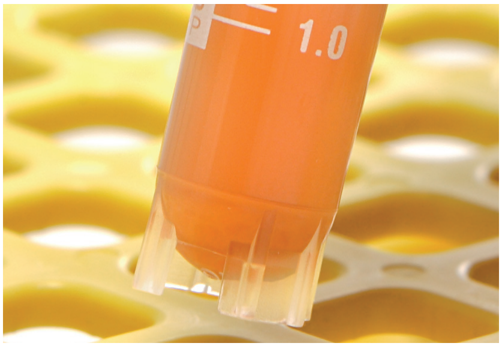

Figure 2

Suspension

Instrumentation

All measurements were performed using the bench top TXRF spectrometer S2 PICOFOX. This instrument is equipped with an air-cooled low power X-ray tube (W target), a multilayer monochromator with 80% reflectivity and the liquid nitrogen-free XFlash® Silicon Drift Detector (SDD) with an energy resolution of < 150 eV (Mn Kα).

Sample preparation and measurements

The following liquid samples were chosen for analysis using TXRF with W excitation:

- ICP multi-element standard "Merck XVI"
- Pharmaceutical caffeine, dissolved in distilled water and spiked with several mono-element standards

The following solid samples were selected:

- Reference sample "NIST 2556" (recycled autocatalyst)
- Multi-element reference standard QC-21
- Reference soil sample CN-SO-01

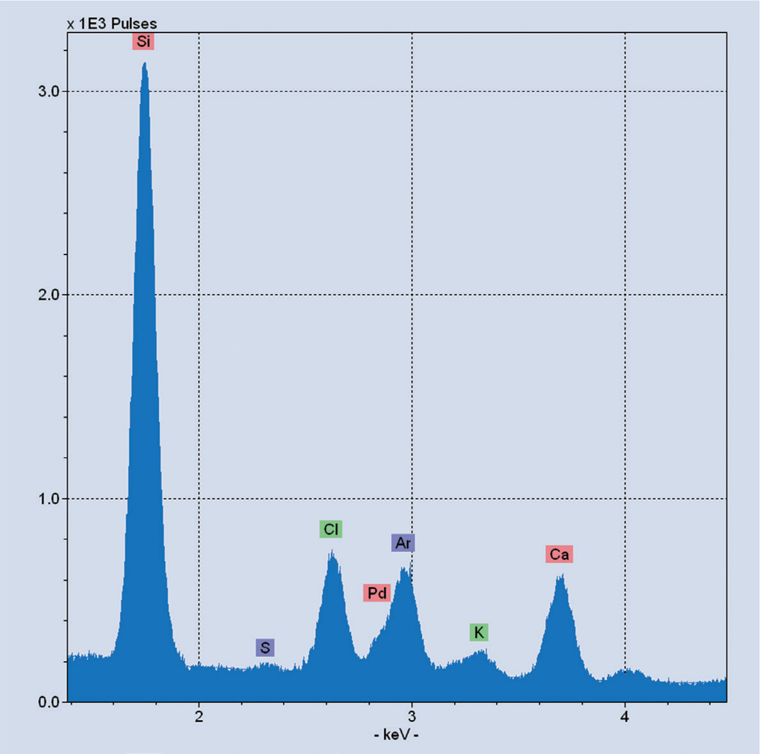

Figure 3
TXRF measurement using Mo excitation. Sample: aspirin suspension spiked with 50 µg/g Pd, calculated detection limit = 2.5 µg/g

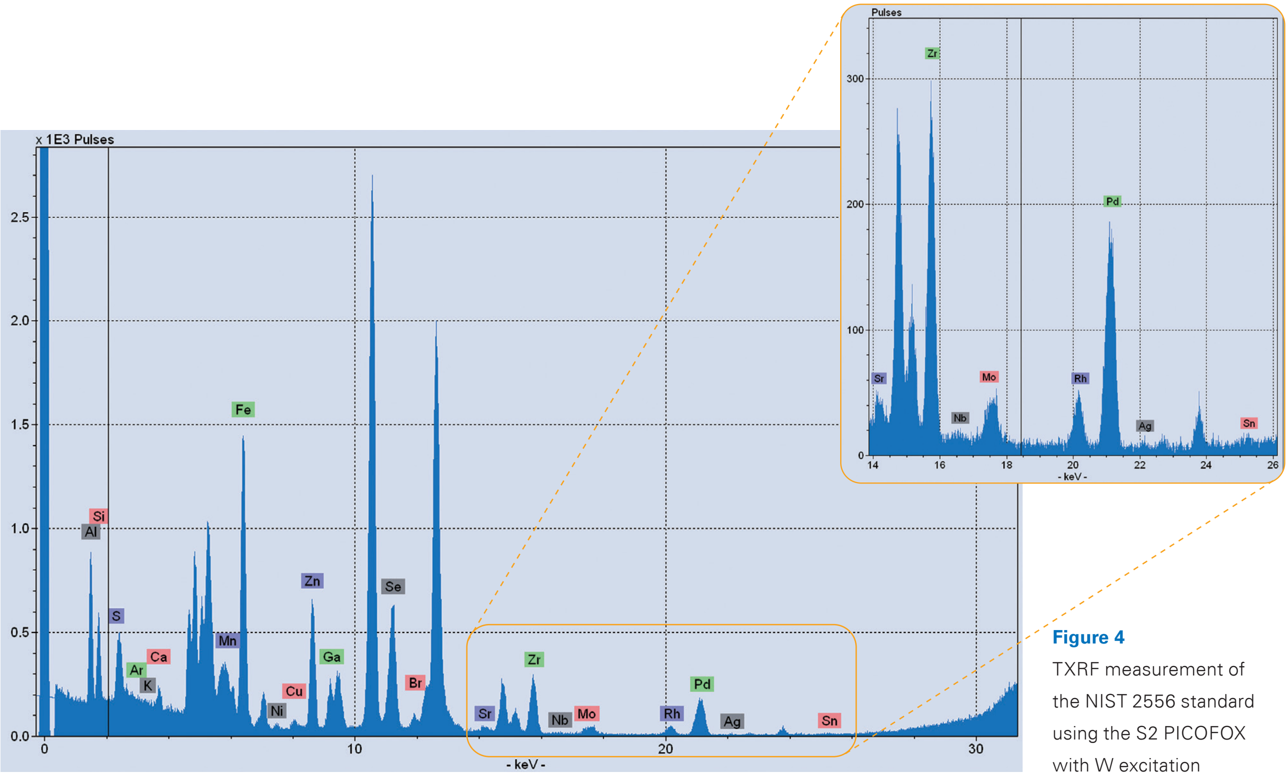

Figure 4
TXRF measurement of the NIST 2556 standard using the S2 PICOFOX with W excitation

Liquid samples were prepared by addition of 10 µl mono-element standard solution to aliquots of 1 ml sample. After thorough homogenization 10 µl of the solution were transferred to a quartz glass sample carrier and dried in vacuum.

Solid samples were prepared as suspensions after careful grinding. About 20 – 50 mg of the solid sample was suspended in aqueous (1 vol.-%) Triton X100 solution. After internal standardization with a mono-element standard and subsequent homogenization 10 µl of the suspension was prepared on a quartz glass carrier in the same way as the liquid samples.

All samples were measured as duplicates with the parameters listed in Table 1.

Results

The comparison of TXRF measurement results for selected elements with the reference values is displayed in Figures 5 and 6.

In general, the measured values are in good concordance with reference values of liquid samples. For solid samples the deviation depends strictly on the particle size. The use of an appropriate mill is highly recommended.

The detection limits, when applying W-excitation, are distinctly higher compared to those for Mo-excitation (Figure 6). This is mainly caused by a less efficient Bremsstrahlung excitation and the lower detection efficiency of the SDD for high-energetic fluorescence radiation.

Typical values are in the tenth to hundredth ppb range for liquid samples or in the ppm range for solid samples and suspensions. As mentioned before the grain size of the solid particles shows a significant influence when using the W-excitation. The measurement results of the solid samples were gained by particle sizes of < 10 µm for pigments, but < 75 µm in case of the catalyst and soil samples.

Tube settings		**Measurement time**
HV	**Current**	
50 kV	1000 µA	2000 s

Table 1
TXRF measurement parameters for W excitation

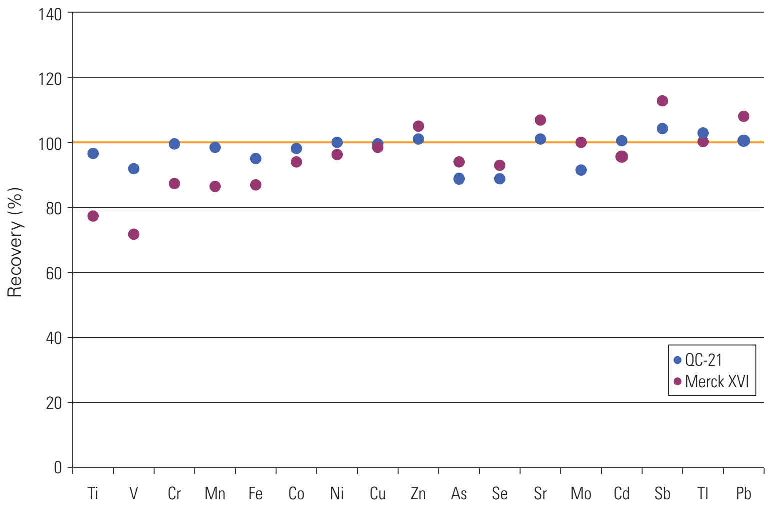

Figure 5
Element recovery results shown for liquid standards using the TXRF spectrometer S2 PICOFOX with a W tube

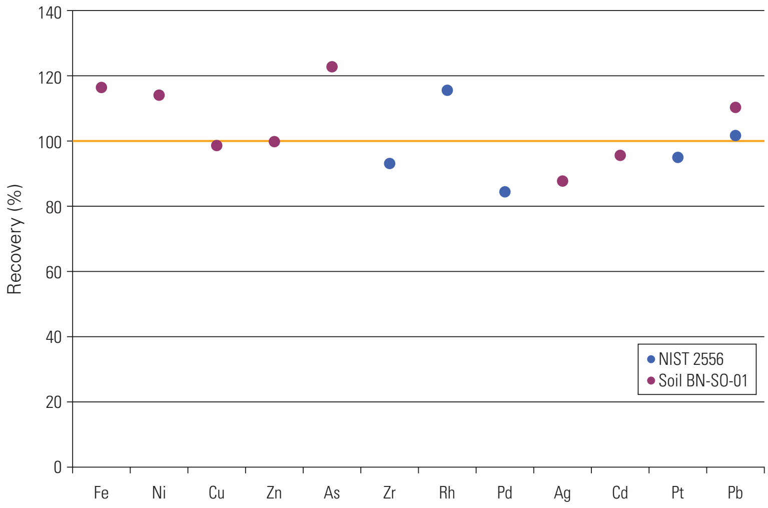

Figure 6
Element recovery results shown for solid standards using the TXRF spectrometer S2 PICOFOX with a W tube

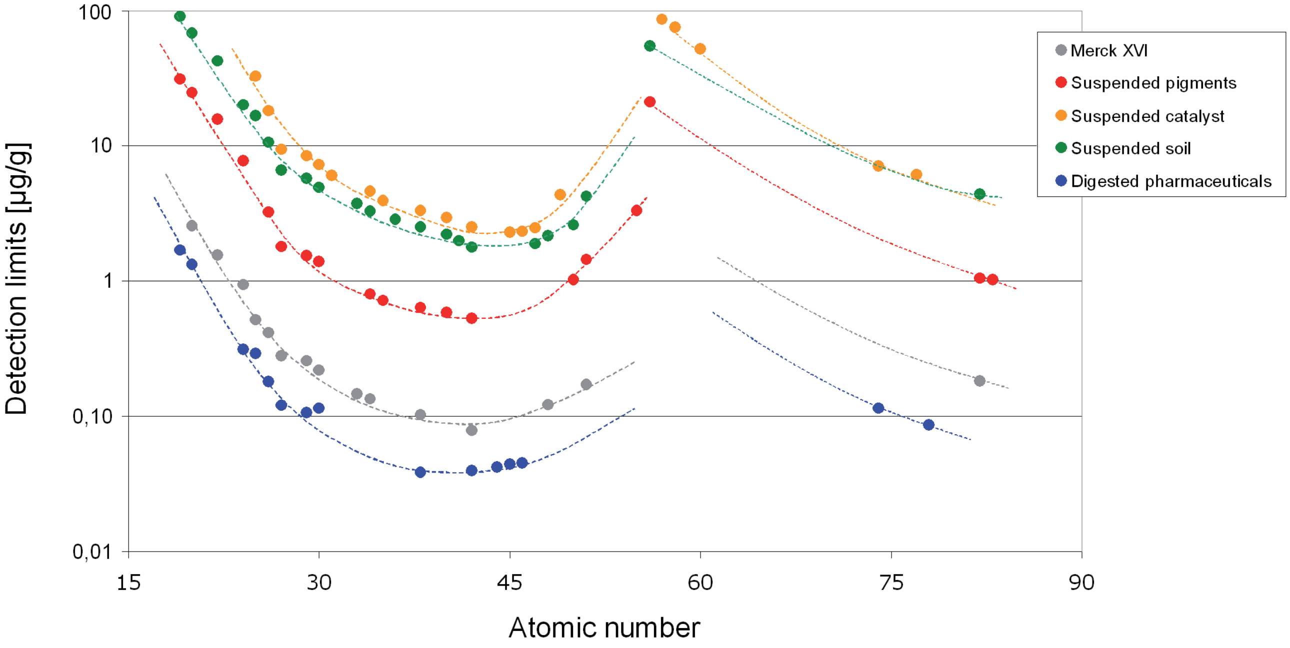

Figure 7

Detection limits for liquid and solid standard samples applying a W tube for TXRF measurements

Conclusion

The measurement data presented in this paper clearly demonstrate the suitability of the S2 PICOFOX with W-excitation for trace analysis of elements like Cd and Pd, which can not be analyzed with Mo-excitation.

Even though the sensitivity of the version with Mo-excitation is significantly higher, most analytical tasks can be solved with the W-excitation version through adequate sample preparation.

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