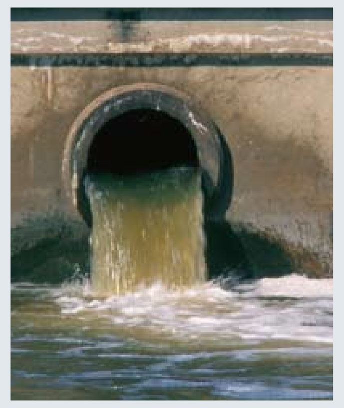
Sample Types and Preparation for TXRF

Water



Sample Type and Examples

Water

Potable, river, rain, sea and waste water

Pure chemicals

Acids, bases, solvents

Sample Preparation

The basic procedure

- Fill micro reaction tube with 1 ml sample
- Add 5 µl internal standard (IS) solution (Ga, 100 mg/L, end concentration 500 µg/L) and homogenize
- Pipette 10 µl on a siliconized sample carrier and dry by heat (60 °C) or vacuum

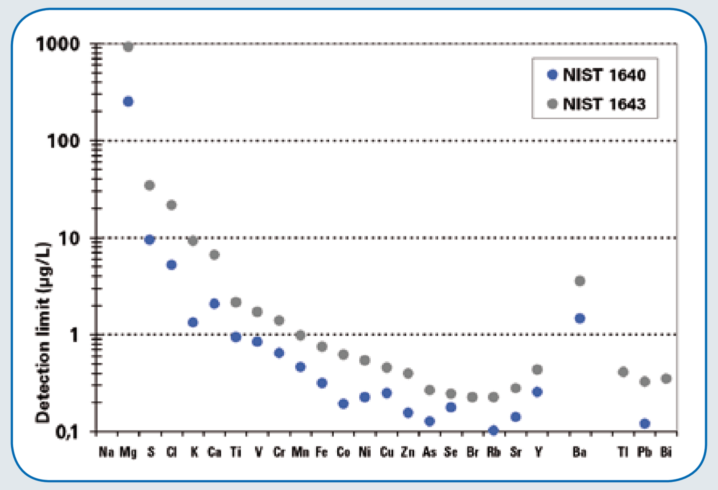
Avoid contamination

- Use a laminar flow box as working place with air filtration for a contamination-free preparation and storage of samples and equipment
- Store sample discs in suitable containers. During preparation open these containers and other tubes and vials just as long as necessary

Remarks

- The maximum sample volume applied on a carrier is about 20 µl, the minimum volume depends on the precision of the pipette
- Multiple pipetting/drying cycles for sample enrichment are possible

Detection Limits



Detection limits for NIST fresh water reference standard

TXRF Benefits

- Detection limits down to 0.1 µg/L
- Total element content of solution and particulate matter will be determined

Body fluids

Sample Type and Examples

Body fluids

Blood, serum, urine

Salted fluids, beverages

Sea, waste water, wash solutions, juices

Sample Preparation

Fast dilution procedure

- Dilute a sample aliquot with 0.2 Vol.-% PVA or ultrapure water (whole blood 1:1, serum 1:5)
- Add 10 µl IS solution (Ga, end conc. 0.2 mg/L) and homogenize
- Blood samples: pipette 10 µl on an untreated sample carrier and dry by heat (60 °C)
- Salt water: pipette 10 µl on a siliconized sample carrier, dry by vacuum and measure Cl, Br. Afterwards, the Cl matrix can be removed with 5 µl HNO_3 and subsequent heating.

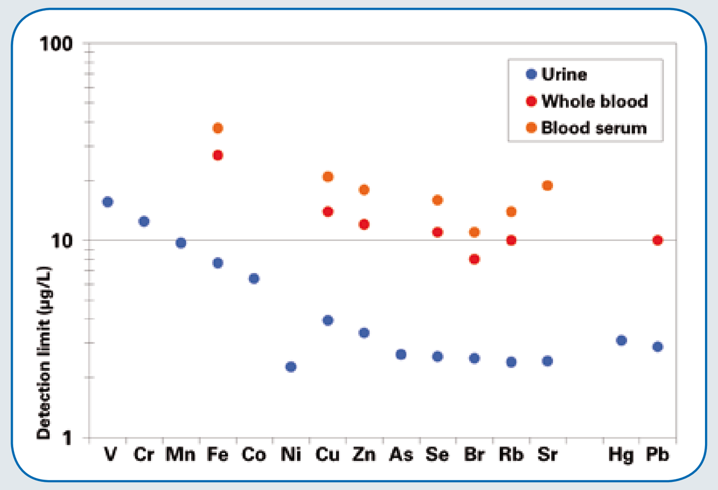
Samples with volatile elements

- For samples containing volatile elements the use of fixation agents is recommended
- Hg: add a 0.01 M thiourea solution in a ratio of 1:1 and dry by air in a clean bench

Remarks

- In case of small sample amounts the internal standard (IS) is used for dilution
- Example: 10 µl of whole blood is diluted with 10 µl of IS solution (0,4 mg/L). After homogenization 10 µl of the mixture is pipetted on a carrier

Detection Limits



Detection limits for urine, whole blood and serum of non-digested reference standards

TXRF Benefits

- Detection limits below 20 µg/L for metals
- Fast sample preparation by a simple dilution step, no digestion required

Tissues

Sample Type and Examples

Tissues

Homogenates of hair, kidney, liver, lung

Multi-phase mixtures

Liquid nutrients, food homogenates

Sample Preparation

Fast dilution procedure

- Dilute 500 µl of the sample (homogenate) with 0.2 Vol.-% PVA water (1:1)
- Add 10 µl IS solution (Ga, 50 mg/L, end conc. 0.5 mg/L) and homogenize
- Pipette 10 µl on a siliconized sample carrier and dry by heat or air

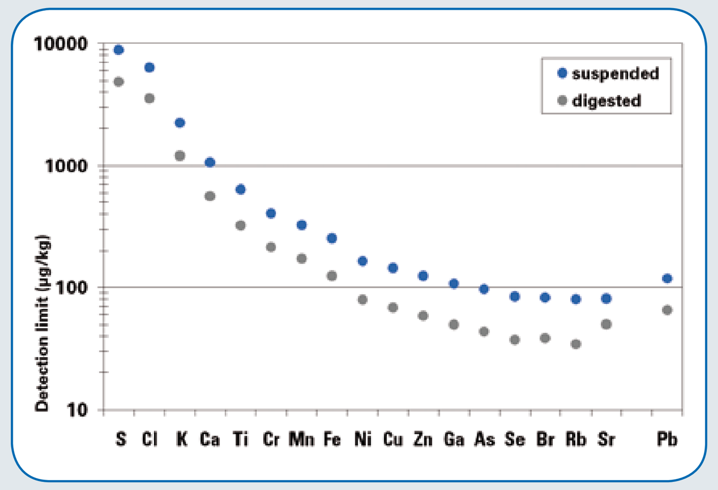
Digestion procedure

- Add 100 µl conc. nitric acid to 400 µl sample and heat to 70 °C for 1 hour
- After cooling add 10 µl IS solution (Ga or Y, 25 mg/L, end conc. 0.5 mg/L) and homogenize
- Pipette 10 µl on a siliconized sample carrier and dry by heat or air

Remarks

- Alternatively a fast disruption procedure can be applied to tissues:
  – Treat tissue in buffer in an ultrasonic bath
  – Separate particles by centrifugation
  – Add IS to supernatant and transfer to disc

Detection Limits

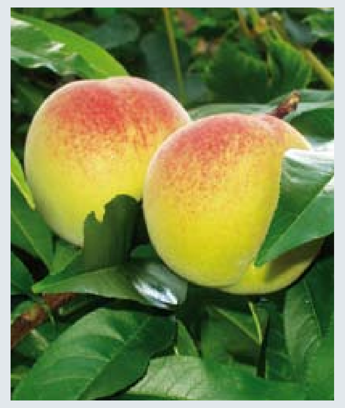


Detection limits for fish standards prepared as suspension or after digestion

TXRF Benefits

- Fast sample preparation by a simple dilution step possible; improved detection limits after treatment with nitric acid
- High linear range from 50 ppb to 5 %

Plant and wooden material



Sample Type and Examples

Plant and wooden material

Algae, leaves, braid, moss, needles, roots

Food and nutrients

Fish, meat, vegetables

Sample Preparation

Quantitative procedure without digestion

- Grind dried sample in a mortar or ball mill
- Weigh about 50 mg in a tube and add 2.5 ml 1 Vol.-% aqueous Triton X-100 solution
- Add 10 µl IS solution (Ga, 1 g/L, end conc. 200 mg/kg) and homogenize in an ultrasonic bath for 15 min
- Pipette 10 µl on a siliconized sample carrier and dry by vacuum

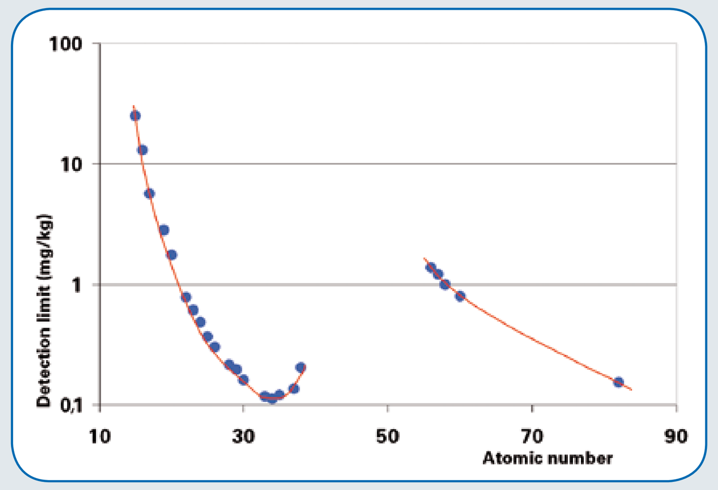
Procedure for micro samples

- Weigh the sample in a micro cup with an ultra-balance and note the exact weight
- Add 500 µl Triton X-100 and 10 µl internal standard (Ga, 100 mg/L, end conc. 20 mg/kg)
- Homogenize, load carrier with 10 µl suspension

Remarks

- Triton X-100 is a common detergent, which is used to adjust the viscosity of aqueous solutions
- For matrix-rich samples the calibration for light elements (Z<20) should be optimized

Detection Limits



Detection limits for plant standards prepared as suspension

TXRF Benefits

- Preparation of a suspension after grinding avoids time-consuming digestion
- Easy analysis of wet and lubricious samples

Oils, pigments

Sample Type and Examples

Oils, pigments

Fuels, crude oil, fat, grease, creams, inks

Thin layers

Contaminations, films, foils, precipitates

Sample Preparation

Semi-quantitative analysis of thin layers

- Cut out a 5x5 mm section of the thin layer with a ceramic knife
- Fix the section on the center of the carrier with some ultrapure vacuum grease
- Standardless quantification mode delivers relative element ratios

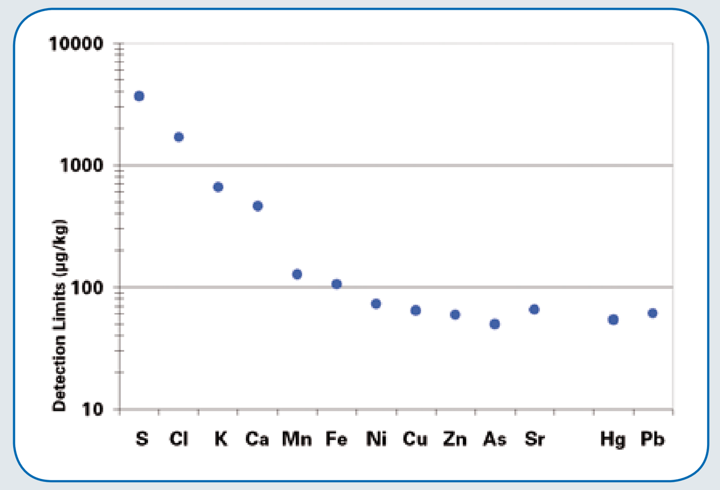
Quantitative extraction of thin layers

- Put filter in a 7 ml THF vessel (e.g. Savilex), add 2 ml HNO_3 (p.a.) and 20 µl Se IS solution (1 g/L)
- Place in an ultraconic bath for 15 min
- Rinse filter with 1 ml HNO_3, homogenize and transfer 10 µl to sample carrier

Remarks

- For the analysis of oils and greases a pipette might not be suitable:
  – Weigh about 500 mg dissolved or liquid sample
  – Add 20 µl organic IS (1 g/L) and homogenize
  – Wipe a thin sample film on the disc (cotton bud)
  – Measure without drying

Detection Limits



Detection limits for industrial grease samples dissolved in organic solvents

TXRF Benefits

- Due to the high sensitivity of TXRF, the "organic film" method delivers instant results
- Non-destructive measurements of films and foils possible

Soils, minerals

Sample Type and Examples

Soils, minerals

Sediments, sewage sludge, ores, silicates

Particles, hi-tech materials

Fines, nanoparticles, aerosols, flue-ash

Sample Preparation

Quantitative procedure without digestion

- Grind sample in a mortar or ball mill
- Weigh about 50 mg in a tube and add 2.5 ml 1 Vol.-% aqueous Triton X-100 solution
- Add 10 µl IS solution (Se, 1 g/L, end conc. 200 mg/kg) and homogenize in an ultrasonic bath for 15 min
- Pipette 10 µl on a siliconized sample carrier and dry by vacuum

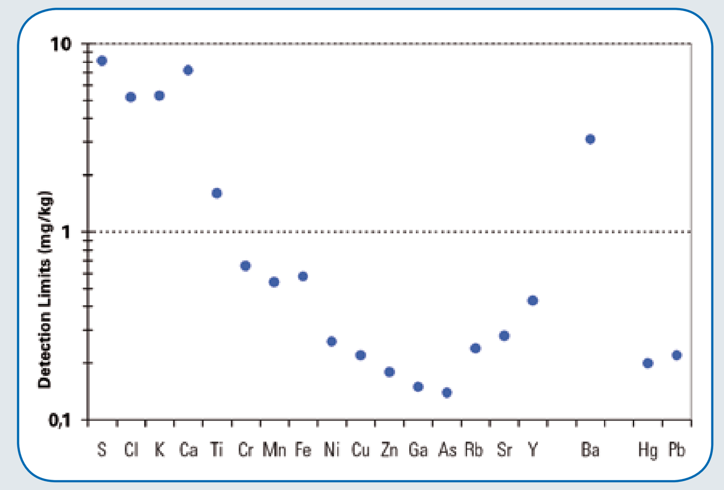
Procedure for determination of element ratios

- Transfer some particles (recommended size <20 µm) to the center of the carrier, fix with vacuum grease, if necessary
- Apply for direct measurement without further treatment

Remarks

- Quantitative TXRF analysis of particles: particle size must be below 70 µm, for best accuracy a size of <20 µm is recommended
- The representativity of small amounts of inhomogenous samples might be limited

Detection Limits



Detection limits for glass samples prepared as suspension

TXRF Benefits

- Extremely fast preparation for determining relative element ratios of particles
- Fast element screening prior to an ICP-MS measurement (Bruker 820-MS)

Golden Rules of TXRF

Siliconization of quartz carriers

- For aqueous samples the quartz carriers need to be siliconized
- Pipette a droplet of silicon solution (e.g. Serva™) and dry. The hydrophobic surface avoids spreading of the sample.

Sample preparation on carriers

- Pipette sample in the centre of the carrier
- Slightly agitate suspensions when pipetting
- After drying the sample, spot size should not exceed 100 µm in height and ø 10 mm
- Acids need to be evaporated completely

Sample drying

- By vacuum in a desiccator (not suitable for blood and tissues)
- By heat in an oven at 60 °C
- On a Ceran™ heat plate; avoid contamination by covering the discs with a petri dish

Sample vessels and reagents

- Avoid the use of colored tubes and gloves, which may contain metal traces
- We recommend to work with reusable vessels and beakers made of PTFE
- PVA: Polyvinyl alcohol acts as a film former and leads to flat, homogenous sample films

Bruker Nano GmbH
Berlin · Germany
Phone +49 (30) 670990-0
Fax +49 (30) 670990-30
info@bruker-nano.de

www.bruker.com

Bruker AXS GmbH
Karlsruhe · Germany
Phone +49 (7 21) 5 95-28 88
Fax +49 (7 21) 5 95-45 87
info@bruker-axs.de

Bruker AXS Inc.
Madison, WI · USA
Phone +1 (608) 276-3000
Fax +1 (608) 276-3006
info@bruker-axs.com

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