## Challenge

Determination of Cd, Pb, Ni, Cu, Mn, Zn and Cr in sewage sludge.

## Solution

Reliable routine analysis using flame AAS on the novAA 800 F.

# Determination of Toxic and Eco-toxic Elements in Sewage Sludge with Flame AAS

### Introduction

A global boom of industrialization and an increasing demand for advanced materials and products is leading to environmental release of harmful and even toxic compounds in many regions of the world.

Toxic metals, such as cadmium, lead or chromium as well as high concentrations of other potentially harmful elements, e.g. nickel or copper, often pass into eco systems through sewage sludge from industrial sites, as well as from weathering or wearing of pipes, reactors and other industrial facilities. Hence, a close monitoring of sewage sludge is the key to meeting statutory limits, and to allow targeted intervention in case of potential hazards.

This application note describes a straight-forward and robust flame AAS method for routine analysis of cadmium, lead, nickel, copper, manganese, zinc, and chromium in sewage sludge for industrial QC labs with moderate sample loads.

analytikjena
An Endress+Hauser Company

## Materials and Methods

### Samples and Reagents

- Reference materials for sewage sludge, BCR 143R, and BCR 146R

Two reference materials for sewage sludge with known analyte concentrations were analyzed for method validation.

### Sample Preparation

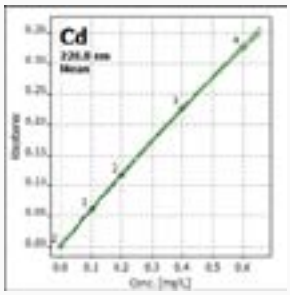
The sample was prepared according to ISO 15587-1 using the microwave system TOPwave (vessel type PM60). Approximately 0.5 g of the reference sample was digested in 6 mL aqua regia as digestion agent, transferred to a graduated flask and filled up to 50 mL with deionized water. If the extraction of potential fumes during the aqua regia digestion cannot be ensured, ISO 15587-2 using nitric acid as digestion agent can be applied as well. Alternatively, the sample can be digested in a beaker on a hot plate. However, silicones or certain organic compounds of the sewage sludge may not be completely digested in this case.

### Calibration

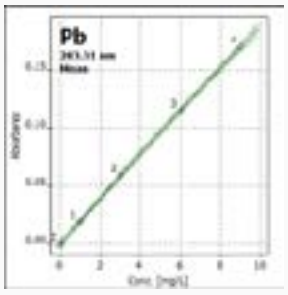
A standard calibration was applied and standards were prepared manually using 1 % HCl and 0.1 % $CsCl/LaCl_3$. Alternatively, the standards can be prepared by the autosampler from a stock solution using the automated dilution function. The limit of quantification (LOQ) was calculated from 3 times the limit of detection (LOD). The method-specific limit of detection (LOD) was calculated from the 3-fold standard deviation of the 11-fold measurement of the digestion blank.

Table 1: Concentration of calibration standards

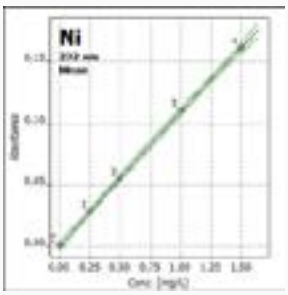
| Standard | Concentration [mg/L] | | | | | | |
|---|---|---|---|---|---|---|---|
| | Cd | Pb | Ni | Cu | Zn | Mn | Cr |
| Cal. 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Cal. Std. 1 | 0.1 | 1 | 0.25 | 0.5 | 0.1 | 0.2 | 0.5 |
| Cal. Std. 2 | 0.2 | 3 | 0.5 | 1 | 0.2 | 0.5 | 1 |
| Cal. Std. 3 | 0.4 | 6 | 1 | 1.5 | 0.4 | 1 | 2 |
| Cal. Std. 4 | 0.6 | 9 | 1.5 | 2 | 0.5 | 1.5 | 3 |



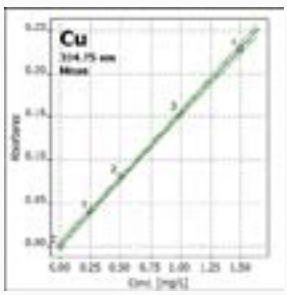

Non-linear rational
$R^2$ = 0.9999
LOQ = 0.003 mg/L



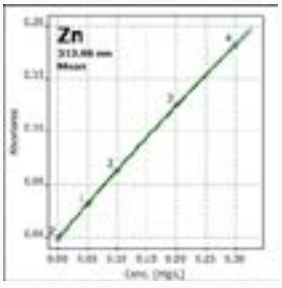

Non-linear rational
$R^2$ = 0.9997
LOQ = 0.024 mg/L



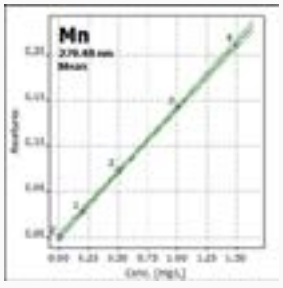

Linear
$R^2$ = 0.9995
LOQ = 0.094 mg/L



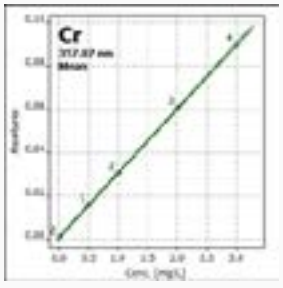

Linear
$R^2$ = 0.9991
LOQ = 0.012 mg/L




Non-linear rational
$R^2$ = 0.9999
LOQ = 0.003 mg/L




Non-linear rational
$R^2$ = 0.9992
LOQ = 0.115 mg/L




Non-linear rational
$R^2$ = 0.9999
LOQ = 0.102 mg/L

Fig. 1: Calibration Curves

### Instrumentation

The measurements were performed using a novAA 800 F for flame AAS, equipped with injection switch SFS 6.0 and an autosampler with automatic dilution function. The analysis was carried out using a 100 mm burner head for air/acetylene flame and a 50 mm burner head for air/nitrous oxide flame.
The use of an automatic burner head cleaner, the Scraper, allows automated removal of deposits from the burner slit at regular intervals when using the nitrous oxide flame.

### Instrument Settings and Method Parameters

Table 2: Instrument settings and method parameters

| Element | Wavelength [nm] | Slit [nm] | Lamp current [mA] | Burner with [mm] | Burner height [mm] | Flame type | Fuel gas flow [L/h] |
|---|---|---|---|---|---|---|---|
| Cd | 228.8 | 1.2 | 2 | 100 | 9 | $C_2H_2$/air | 40 |
| Pb | 283.3 | 1.2 | 4 | 100 | 7 | $C_2H_2$/air | 50 |
| Ni | 232.0 | 0.2 | 5 | 100 | 7 | $C_2H_2$/air | 50 |
| Cu | 324.7 | 1.2 | 5 | 100 | 6 | $C_2H_2$/air | 45 |
| Zn | 213.9 | 0.8 | 2 | 100 | 5 | $C_2H_2$/air | 50 |
| Mn | 279.5 | 0.2 | 5 | 100 | 9 | $C_2H_2$/air | 55 |
| Cr | 357.9 | 0.8 | 4 | 50 | 5 | $C_2H_2/N_2O$* | 210 |

* Cr as a refractory metal requires higher atomization temperatures, hence a $C_2H_2/N_2O$ gas mixture and a 50 mm burner head may benefit the Cr analysis

## Results and Discussion

The analysis results (Table 3) for the two certified reference materials of industrial sewage sludge, BCR 143R and BCR 146R, show very good agreement of 94-103% with the certified values. All elements could be quantified by external calibration with aqueous standards in diluted or undiluted samples.

Table 3, Part 1: Measurement result

| Sample | Element | Dilution factor | Measured concentration [mg/kg] | RSD [%] | Certified concentration [mg/kg] | Revovery rate [%] |
|---|---|---|---|---|---|---|
| Sewage sludge BCR 143 R | Cd | 3 | 71.8 | 0.6 | 72.0 | 100 |
| | Pb | 2 | 174 | 3.7 | 174 | 100 |
| | Ni | 3 | 290 | 3.4 | 296 | 98 |
| | Cu | 2 | 125.7 | 0.6 | 128 | 96 |
| | Zn | 50 | 1061 | 2.5 | 1063 | 100 |
| | Mn | 15 | 848 | 0.6 | 858 | 99 |
| | Cr | 4 | 419 | 1.2 | 426 | 98 |

Table 3, Part 2: Measurement result

| Sample | Element | Dilution factor | Measured concentration [mg/kg] | RSD [%] | Certified concentration [mg/kg] | Revovery rate [%] |
|---|---|---|---|---|---|---|
| Sewage sludge BCR 146 R | Cd | 2 | 18.7 | 0.8 | 18.4 | 102 |
| | Pb | 2 | 554 | 2.0 | 583 | 95 |
| | Ni | 1 | 64.9 | 2.8 | 65 | 100 |
| | Cu | 10 | 817 | 0.8 | 831 | 98 |
| | Zn | 200 | 2975 | 1.9 | 3040 | 98 |
| | Mn | 10 | 299 | 2.1 | 298 | 100 |
| | Cr | 2 | 179 | 1.9 | 174 | 103 |

## Conclusion

The novAA 800 F allows fast, simple and highly precise determination of cadmium, lead, nickel, copper, zinc, manganese, and chromium in pre-digested sewage sludge samples. Very good agreement of the results with the values of two certified reference materials (95-103%) as well as low standard deviations prove validity of the analysis procedure including the microwave-assisted digestions and therewith the high method robustness in high matrix samples.

The SFS 6.0 injection switch with continuous rinsing function and segmented sample injection ensures reduced carryover in case of high salt and matrix content while the automatic cleaning of the burner head using the Scraper provides stable analysis conditions for highly reproducible results. Using the autosampler with integrated dilution function enables a high sample throughput even for high matrix samples.

This document is true and correct at the time of publication; the information within is subject to change. Other documents may supersede this document, including technical modifications and corrections.

**Headquarters**
Analytik Jena GmbH
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

Version: 2.0 I Author: AnJu
en · 01/2021
© Analytik Jena GmbH | Pictures ©: Pixabay/falco