Challenge

Routine analysis of Cd, Cu, Ni, Pb, Zn, and Cr in wastewater and sewage sludge in a treatment plant.

Solution

Fast-sequential analysis using contrAA 800 in flame mode and autosampler AS-FD for full automation.

Fast-sequential Analysis of Toxic Elements in Wastewater and Sewage Sludge by HR-CS AAS

Introduction

In municipal and industrial treatment plants, many different wastewater samples from various inlets, outlets, and pumping stations within the wastewater treatment plant as well as samples from different industrial dischargers must be analyzed regularly. Relevant analytes include many toxic and ecotoxic elements, such as cadmium, copper, nickel, lead, zinc, and chromium. While the concentration of heavy metals in household wastewater is usually rather low, it can be very high in industrial effluents. In addition to wastewater, sewage sludge samples are also important. The heavy metal concentration in the sludge determines whether it can be used as a fertilizer in agriculture, needs to undergo separate treatment, e.g., in biogas plants, or even has to be stored as hazardous waste in special landfills. The high matrix content of the samples, especially due to organic components, usually requires a digestion step. Although this successfully destroys the organic matrix, it also introduces a high content of oxidizing acids, e.g., nitric acid, which can cause spectral interference. Matrix effects can also be caused by high concentrations of other elements, e.g., iron.

To meet all these challenges, the demands on the analysis instrument are high. In this application note, we analyzed wastewater and sewage sludge samples from a municipal sewage treatment plant using the contrAA 800 F, which is a high-resolution continuum source flame atomic absorption spectrometer (HR-CS-AAS). The contrAA 800 is able to process many samples with different matrices with a wide range of analytes. It is robust, easy to operate, and fully automated for daily routine operation using the autosampler AS-FD with automatic dilution function. The xenon short-arc lamp emits a continuous spectrum, so that all analysis lines can be used without changing the lamp. Thereby it allows a fast-sequential analysis of several elements with just one sample aspiration. Thus, the analysis of several elements in one sample hardly takes more time than the analysis of a single element. The high intensity of the lamp at all wavelengths allows very low detection limits. For higher concentrated samples an alternative wavelength with lower sensitivity can be selected, thus avoiding the need to dilute the sample.

Materials and Methods

Samples

The samples were supplied by the main sewage treatment plant of a midsized city in Germany. The inlet, the outlet, and two different pump stations of the sewage treatment plant were sampled, as well as wastewater from three different industrial dischargers. In addition, two different sewage sludge samples were analyzed.

Reagents

- Hydrochloric acid, c(HCl) = 32wt-%, ρ(HCl) = 1.16 g/mL
- Nitric acid, $c(HNO_3)$ = 65wt-%, $\rho(HNO_3)$ = 1.39 g/mL
- Hydrogen peroxide solution, $c(H_2O_2)$ = 30 %
- $CsCl/LaCl_3$ buffer (100 g/L each, 5% HCl)
- Certified single element standard solutions of Cd, Cu, Ni, Pb, Zn, and Cr (1000 mg/L each)
- Ultrapure water

Sample preparation

All samples went through a microwave digestion procedure. The wastewater samples were digested with a mixture of nitric acid and hydrogen peroxide, the sewage sludge samples with aqua regia. Before measurement, 0.1wt-% $CsCl/LaCl_3$ buffer (= 1 g/L) was added to each sample. Dilutions were prepared with 1vol-% HCl and 0.1wt-% $CsCl/LaCl_3$ in water.

Instrumentation and method parameters

The analysis was performed with the high-resolution continuum source atomic absorption spectrometer contrAA 800 in flame mode. The instrument was equipped with a 50 mm burner head, the injection switch SFS 6, and an AS-FD autosampler with automatic dilution function. For operation of the nitrous oxide flame, an automatic burner head cleaner, the scraper, was used additionally. The method parameters are shown in Table 1 and the evaluation parameters are shown in Table 2.

Table 1: Method parameters

Element	Wavelength [nm]	Flame type	Fuel gas flow [L/h]	Burner height
Cd	228.8018	C_2H_2/air	45	7
Cu	324.7540	C_2H_2/air	45	6
Ni	232.0030	C_2H_2/air	45	6
Pb	217.0005	C_2H_2/air	50	8
Zn	213.8570	C_2H_2/air	50	7
Cr	359.3488	C_2H_2/N_2O	185	6

Table 2: Evaluation parameters

Element	Measurement time [s]	Evaluation pixel	Spectral observation width		Background correction mode
			[nm]	[pixel]	
Cd	3	5	0.30	200	IBC
Cu	3	5	0.39	200	IBC
Ni	3	5	0.29	200	IBC + LSBC
Pb	3	5	0.28	200	IBC
Zn	3	5	0.27	200	IBC + LSBC
Cr	3	5	0.49	200	IBC

Calibration

All standards were prepared from certified single element standards with a concentration of 1000 mg/L and were diluted with 1 vol-% HCl and 0.1 wt-% $CsCl/LaCl_3$ in water. The calibration curves are shown in Figures 1 to 6 and the concentrations of the calibration standards are given in Table 3.

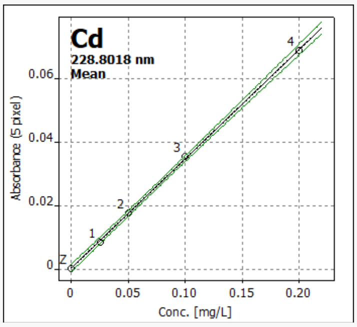

Figure 1: Cd 228.8018 nm
R^2 = 0.9993
LOD = 0.0005 mg/L

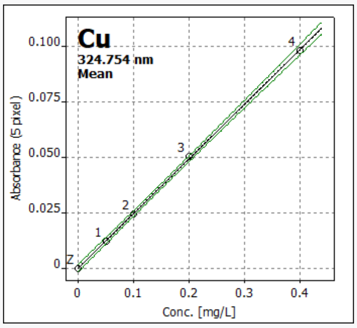

Figure 2: Cu 324.7540 nm
R^2 = 0.9994
LOD = 0.001 mg/L

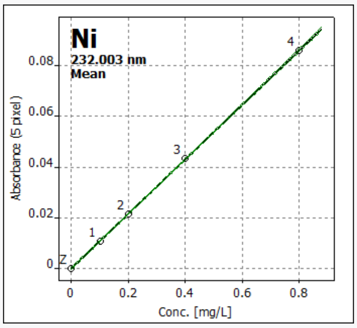

Figure 3: Ni 232.0030 nm
R^2 = 0.9999
LOD = 0.002 mg/L

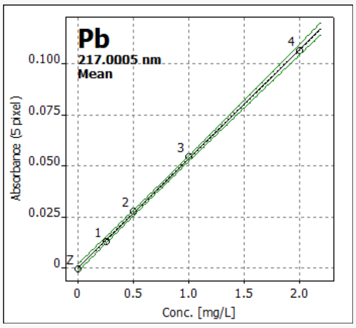

Figure 4: Pb 217.0005 nm
R^2 = 0.9994
LOD = 0.005 mg/L

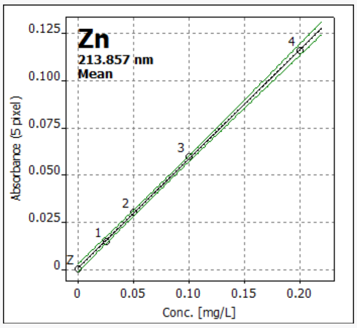

Figure 5: Zn 213.8570 nm
R^2 = 0.9993
LOD = 0.001 mg/L

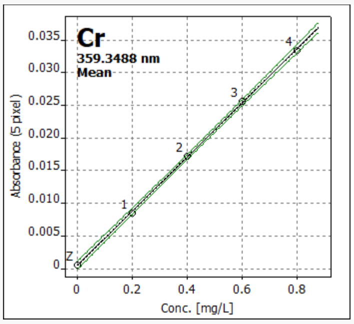

Figure 6: Cr 359.3488 nm
R^2 = 0.9994
LOD = 0.007 mg/L

Table 3: Concentrations of the calibration standards

Standard	Concentration [mg/L]					
	Cd	Cu	Ni	Pb	Zn	Cr
Cal 0	0	0	0	0	0	0
Std. 1	0.025	0.05	0.1	0.25	0.025	0.2
Std. 2	0.05	0.1	0.2	0.5	0.05	0.4
Std. 3	0.1	0.2	0.4	1.0	0.1	0.6
Std. 4	0.2	0.4	0.8	2.0	0.2	0.8

Spectral vicinity and correction

Example spectra of all analytes, recorded during the sample measurements, are shown in Figures 7 to 12. In some spectra, additional lines caused by iron can be seen in the spectral vicinity of the analyte line. However, these lines are well resolved from the analyte line and therefore do not cause spectral interferences. All spectra were corrected automatically with the iterative background correction (IBC) mode. For nickel and zinc, an additional spectral correction using the least squares background correction (LSBC) method was applied to eliminate spectral interferences caused by nitric acid. The correction spectra of nitric acid used for this purpose as well as the original and corrected spectra for zinc are shown as an example in Figures 13 to 15.

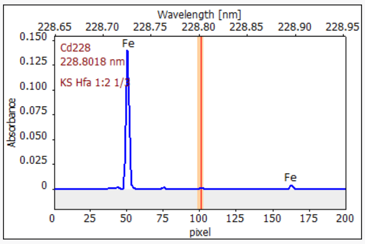

Figure 7: Spectrum of Cd in sewage sludge 1 corrected with IBC

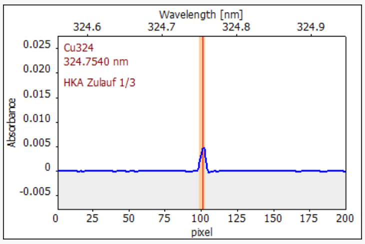

Figure 8: Spectrum of Cu in inlet wastewater corrected with IBC

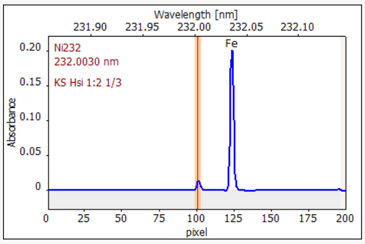

Figure 9: Spectrum of Ni in sewage sludge 2 corrected with IBC

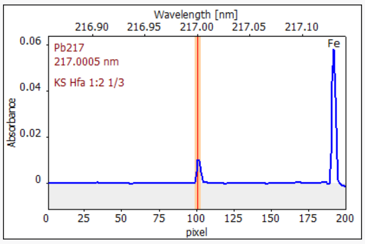

Figure 10: Spectrum of Pb in sewage sludge 1 corrected with IBC

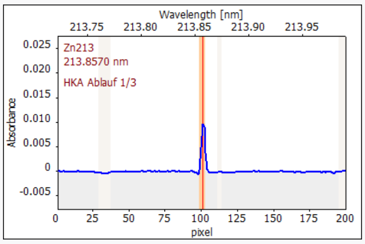

Figure 11: Spectrum of Zn in outlet wastewater corrected with IBC and LSBC

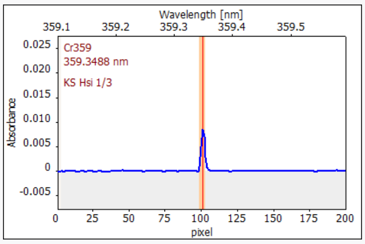

Figure 12: Spectrum of Cr in sewage sludge 2 corrected with IBC

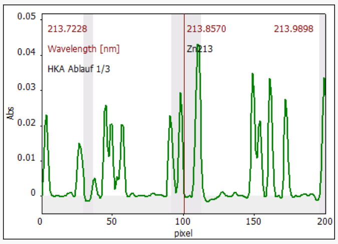

Figure 13: Correction spectrum of NO (diluted HNO_3) used for Zn

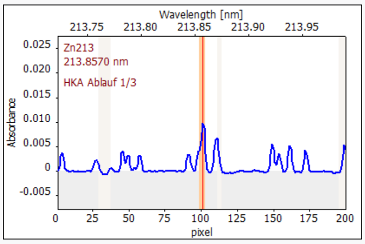

Figure 14: Uncorrected spectrum of Zn in wastewater

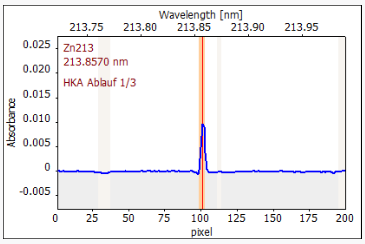

Figure 15: Corrected spectrum of Zn in wastewater with LSBC

Quality control and validation

The limits of detection (LOD) for this method were determined for all elements via the blank value procedure, in which the reagent blank, which contained all reagents used for microwave digestion and dilution, was measured eleven times. For quality control and validation, spiking experiments were conducted for all elements with one wastewater sample and one sewage sludge sample, respectively, and recovery rates were determined.

Results and Discussion

The results for the wastewater samples are shown in Table 4. The concentrations of lead and cadmium were below the detection limit in all samples. For all other elements, small but measurable concentrations from 0.01 mg/L to 0.15 mg/L were determined in all samples. The precision was very high for these low concentrations with RSD values from 0.1% to 5.5%. The inlet, outlet, and pump station samples as well as two of the industrial wastewater samples were measured directly without dilution, while the third industrial sample with a concentration of 0.4 mg/L zinc required a dilution by a factor of 10.

The concentrations in the sewage sludge samples (Table 5) ranged from 0.4 mg/kg for cadmium up to 603 mg/kg for zinc. None of the samples was below the detection limit. For the analysis of copper and zinc, the samples were diluted by a factor of 200, for cadmium, nickel, lead, and chromium by a factor of 2. The precision was excellent with standard deviations from 0.3% to 1.6%.

In the spiking experiments of wastewater and sewage sludge samples (Table 6), recovery rates between 92.5% and 108% were reached. These results show that there were no interfering matrix effects and prove the validity of the method.

Table 4: Results for wastewater samples

Sample	Element	Pre-dilution factor	Concentration in original sample [mg/L]	RSD** [%]
Inlet	Cd	1	< 0.0005*	-
	Cu	1	0.083	0.8
	Ni	1	0.015	2.5
	Pb	1	< 0.005*	-
	Zn	1	0.12	0.4
	Cr	1	0.026	3.8
Outlet	Cd	1	< 0.0005*	-
	Cu	1	0.023	1.5
	Ni	1	0.018	1.5
	Pb	1	< 0.005*	-
	Zn	1	0.046	1.3
	Cr	1	0.033	5.5
Pump station 1	Cd	1	< 0.0005*	-
	Cu	1	0.048	0.4
	Ni	1	0.019	1.5
	Pb	1	< 0.005*	-
	Zn	1	0.069	0.5
	Cr	1	0.043	4.2
Pump station 2	Cd	1	< 0.0005*	-
	Cu	1	0.053	1.1
	Ni	1	0.022	1.0
	Pb	1	< 0.005*	-
	Zn	1	0.063	1.2
	Cr	1	0.039	5.2
Industrial discharger 1	Pb	1	< 0.005*	-
Industrial discharger 2	Cu	1	0.145	1.3
Industrial discharger 3	Zn	10	0.389	0.1

*) Limit of detection (LOD), determined via blank value procedure with eleven measurements of reagent blank

**) RSD = Relative Standard Deviation for three repetition measurements

Table 5: Results for sewage sludge samples

Sample	Sample weight per 100 mL [g]	Element	Pre-dilution factor	Measured concentration [mg/L]	Concentration in original sample [mg/kg]	RSD [%]
Sewage sludge 1	4.46	Cd	2	0.0095	0.427	1.1
		Cu	200	0.060	270	0.5
		Ni	2	0.320	14.4	0.5
		Pb	2	0.556	25.0	0.7
		Zn	200	0.128	574	0.3
		Cr	2	0.564	25.3	1.6
Sewage sludge 2	4.62	Cd	2	0.011	0.498	1.2
		Cu	200	0.061	265	1.2
		Ni	2	0.362	15.7	0.4
		Pb	2	0.488	21.1	0.9
		Zn	200	0.139	603	0.9
		Cr	2	0.585	25.3	0.9

Table 6: Recovery rates of the QC stock samples

Sample	Element	Expected concentration increase [mg/L]	Recovery rate [%]
Inlet	Cd	0.05	93.1
	Cu	0.1	92.5
	Ni	0.2	93.3
	Pb	0.5	95.6
	Zn	0.05	95.2
Sewage sludge 1	Cd	0.05	103
	Cu	0.1	95.8
	Ni	0.2	94.5
	Pb	0.5	105
	Zn	0.05	108
Pump station 2	Cr	0.4	94.1
Sewage sludge 2	Cr	0.4	96.7

Conclusion

With this method, wastewater, and sewage sludge can be analyzed trouble-free. By using a xenon short-arc lamp as continuum source in HR-CS-AAS, all absorption lines in the spectral range of 185 to 900 nm are available for analytical evaluation. This enables the fast-sequential analysis for the elements cadmium, copper, nickel, lead, and zinc in one method, which reduces the measurement time per sample by factor 3 to 4 compared to individual measurements and thus significantly reduces costs. Spectral background is corrected directly on the analysis line, simultaneously and independently of the wavelength used. The spectral environment of cadmium, nickel, and lead shows further absorption lines caused by iron. However, due to the high spectrometer resolution, the signals are clearly separated from each other so that no spectral interference occurs.

When spiking different sample matrices with a defined element concentration as quality control, very good recovery rates of 92.5 to 108% were achieved. This shows the matrix independence of the measurements.

For the determination of chromium, the use of the nitrous oxide flame is recommended, since the higher flame temperature eliminates interferences and thus allows an interference-free analysis without the need to add further reagents. A recommended regular cleaning of the burner head using the additional flame accessory, the scraper, ensures a reliable nitrous oxide flame operation.

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