



Fast and Reliable Analysis of Wastewater and Sludges with A SCANNING ARRAY ICP EMISSION SPECTROMETER

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Introduction

Wastewater and sludge analyses generally require the determination of many elements and are economically performed using ICP-OES, due to the speed and robustness of this technique. Several ICP-OES methods are available for this determination including EPA method 200.7 (1). In the USA, DIN 38 406 E22 (2) in Germany, or ISO 11885 (3) on a global scale.

For this type of application, the concentrations of typical toxicologically-relevant metals to be measured are relatively high compared to the detection limits of this technique. However, the matrix may vary considerably and high matrix concentrations may be observed for some types of samples. In these cases, a matrix-tolerant sample introduction system is as important as hardware and software safeguards in diminishing the effect of unexpected interferences. Array-type ICP emission spectrometers supply the user with spectra rather than single data points (4,5). This allows the user to utilize the spectral information around an analytical wavelength, so spectral interferences can be detected, avoided by selecting an undisturbed line or corrected for. With an array detector, the rate of data acquisition is much faster, because the system does not need to scan between analyte wavelength and background correction points. In

addition, simultaneous background correction yields better precision, contributing to overall accuracy.

The use of ICP-OES in the environmental laboratory ranges from the occasional sample which needs to be run by the technical production workforce to production analyses that occupy the instrument 24 hours a day. Consequently, the requirements on startup and long-term performance are different for each laboratory. Ease-of-use, instant readiness, and robustness of the overall system are some of the considerations in evaluating the instrument.

A new scanning array ICP-OES instrument has been designed, which is able to handle the various demands of environmental analysis. This paper shows the analytical performance of this instrument for wastewater and digested sludges.

Experimental Instrumental

The instrument used was an Optima 2000™ (PerkinElmer Instruments, Norwalk, USA). The spectrometer uses a double-pass Echelle optical mount with movable grating and prism in order to slew to any analytical wavelength. A linear (CCD) as a detector registers the spectrum around the analyte wavelength, which allows simultaneous background correction in order to minimize flicker noise. The detector is

split into two parts, one of which is being used to measure the analyte spectrum while the other registers a neon spectrum which is travelling the same path as the light originating from the plasma. If the system registers deviations from initial settings, then the wavelength setting is actively changed to its original setting, allowing for wavelength stability in the order of 0.1 pm. An example of this wavelength stability is shown in Figure 1.

The system allows the plasma to be viewed either axially or radially. Axial viewing was used in this application to obtain the lowest detection limits.

A newly constructed solid-state RF generator supplies power up to 1500 W with good output stability. For further stabilization of the signal, the sample introduction system can be thermostated for a constant evaporation rate in the nebulizer chamber. The operating conditions are listed in Table 1. The Mg I/II ratio was calculated to be 11.8.

The distance of the injector to the plasma can be adjusted mechanically to optimize performance in the presence of high-dissolved solids. In case of clogging, it is easy to remove the injector from the outside without having to dismount the sample introduction system.

The sample introduction system is mounted on a bayonet system and can easily be removed for routine maintenance. The standard metal-

free GemTip™ cross-flow nebulizer is located on the nebulizer chamber and can be accessed from the outside. The tips can be exchanged without the use of tools. If high-dissolved solids should present a problem, it is advisable to use the GemCone™ nebulizer (6) with cyclonic spray chamber. This type of nebulizer was used with the instrument in a companion paper describing natural runoff from waste dumpsites (7).

The read time was set for a variable range from 1 s to 10 s using the auto-integration mode. This auto-integration feature will take a snapshot of intensity of the line to be measured before the actual reading begins. For high intensities, a short read time will be used, while for low intensities, a longer time will be used. Long measuring times reduce the effect of shot noise and are beneficial in obtaining the lowest detection limits. Depending on the magnitude of the signal, the analysis of 11 elements, run at the conditions stated above, with three replicates, took from 2 min and 20 s to 4 min and 45 s.

Sample Pretreatment

The sludges were digested with aqua regia (DIN S7 method) (2). Three grams of dried sample and 28 mL of aqua regia (21 mL HCl and 7 mL HNO₃, both E. Merck, suprapur) were heated under reflux for three hours and diluted to 100 mL. Two digestions were done of each material.

Calibration Standards

The calibration standard for wastewater was Merck (E. Merck, Darmstadt, Germany) Multielement Standard IV, which was diluted to a final concentration of 1 mg/L. Additional single-element standard solutions were prepared for As, Ba, Mo, and V. Single-element solutions were preferred for these elements rather than adding them or mixing them in order to prevent precipitation (e.g., V available as sulfate

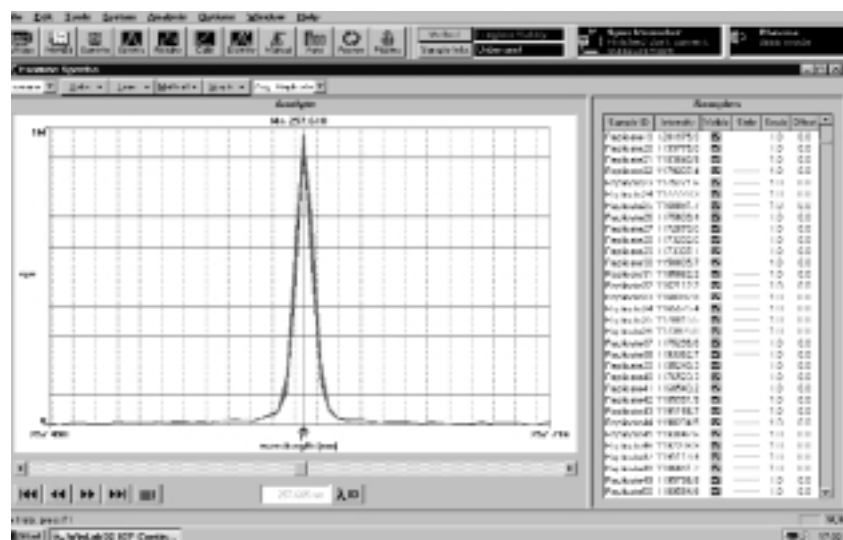


Figure 1: Wavelength stability of the PerkinElmer Optima 2000, at Mn257.610 nm over 8 hours employing active wavelength correction

Table 1: Operating Conditions of the Xscanning Array ICP-OES Optima 2000 for the Analysis of Wastewater and Sludges

RF Power	1300 W
Nebulizer Flow	0.7 L/min
Auxiliary Flow	0.5 L/min
Plasma Flow	15 L/min
Sample Pump Flow	1 mL/min
Plasma Viewing	Axial
Processing Mode	Area
Auto Integration (min – max)	1 – 10 s
Read delay	40 s
Rinse	45 s
Replicates	3
Background correction	Manual, two points
Nebulizer	Cross-Flow
Nebulizer chamber	Scott (Ryton®)
Injector	Alumina, 2 mm

could have caused the precipitation of BaSO₄ or Mo would precipitate if not kept in ammonia solution). Although Ba is contained in Merck IV, a single-element solution was prepared containing 0.1 mg/L, so the calibration standard is in the working range for the very sensitive line at 455 nm when viewed axially. The other elements (As, Mo, and V) were diluted to 1 mg/L.

Calibration for the analysis of sludges was done with matrix-matched standards and blank, which also included the addition of aqua regia (210 mL HCl and 70 mL HNO₃ per 1 L). The main matrix components were also added: Ca 3000 mg/L, Fe 500 mg/L, Al 500 mg/L, and K 100 mg/L. The analytes were added to give a final concentration of 1 mg/L and 10 mg/L.

Results and Discussion

Method Development Considerations

Wavelength Selection

Wavelength selection followed U.S. EPA method 200.7 and ISO regulation 11885 and took into consideration (a) the freedom from spectral interferences, (b) the different sensitivities vs. expected concentrations in the samples. The wavelength selection depends to some extent on the resolution of the spectrometer. Figure 2 shows an example of the resolution for the wavelengths of Cr and Zn near 206 nm, which was found to be at 7.5 pm. Furthermore, the selection of analytical lines was guided by experience gathered with other types of ICP emission spectrometers for this type of application (8-10). In order to cover the different working ranges for water and sludges, two wavelengths were used for Ba: The line at 233 nm for high content in sludges and at 455 nm for lower concentrations in wastewater.

The selected analytical wavelengths are compiled in Table 2. Note that not always the most sensitive line was used in order to avoid spectral interferences. The resolution of the system is sufficiently good to warrant undisturbed measurements for the typical analysis of wastewaters and sludges. A notable exception being the element Cd, where interferences are known on all three known sensitive analytical wavelengths at 214.440, 226.502 and 228.802 nm. While the lines at 214 and 226 nm are interfered by Fe, which can be present in major quantities in some wastewaters and sludges, the line at 228 nm can be disturbed by higher concentrations of As. It is not common to see very high As content in most environmental samples, so this line is the preferred line for this type of application. However, there are rare occasions where the As concentrations are

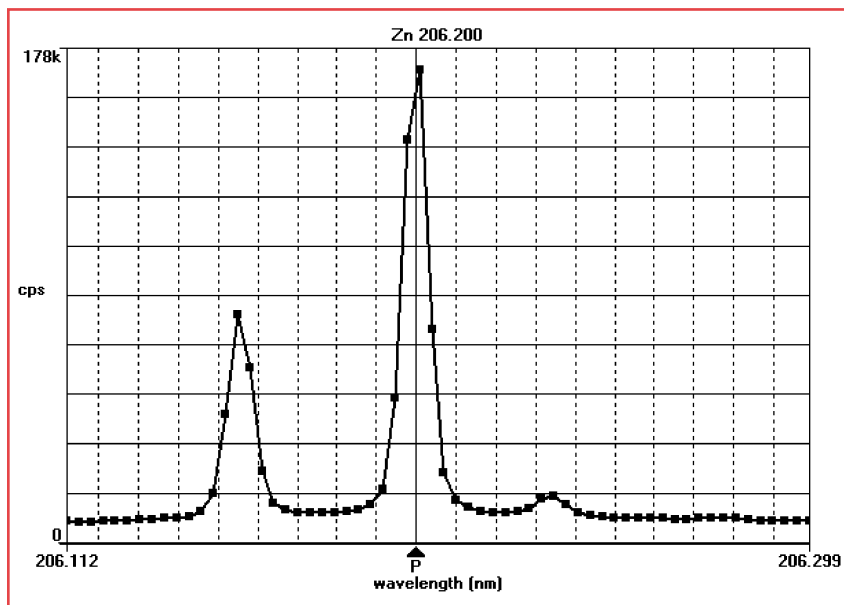


Figure 2: Cr and Zn lines near 206.2 nm measured with a PerkinElmer Optima 2000. The calculated resolution is 7.5 pm.

extremely high, yielding a too high result for Cd, when measured at 228 nm. While the distance between the two lines is 10 pm, the intensity ratio is 20 to 40, Cd being the more sensitive element. As a consequence, an enormous surplus of As will actually cause a false result. E.g., Boumans lists a critical concentration ratio, assuming a resolution of 10 pm (while in fact it is about 8 pm) of 220 (11). This means that a 220-fold surplus of As will result in a signal that is twice as high as the true result. The result depends largely on the way the intensity was calculated from the raw data of the spectrum. It was shown, that for a similar type of application, a chemometric technique, multicomponent spectral fitting (MSF) (12,13) is able to deal with this type of interference best (14). MSF will fit stored model spectra to the measured spectrum. The fitting coefficients will be used for quantification. All that is necessary to apply MSF is to record spectra of all elements contributing in the array. Background correction points need not be set, so the method development for MSF requires less user experience than the conven-

Table 2: Analytical Wavelengths for the Analysis of Wastewaters and Sludges

Element	Wavelength (nm)
Al	396.153
As	197.197
Ba	233.527
Ba	455.403
Be	313.107
Cd	228.802
Co	228.616
Cr	267.716
Cu	327.393
Fe	259.939
Hg	194.168
Mn	257.610
Mo	203.845
Ni	231.604
Pb	220.353
V	292.464
Zn	206.200

tional processing routine. The MSF technique is an integral part of the application software. For this study, the determination of Cd in the presence of As and Fe was examined. As an example, a synthetic solution was prepared containing: Cd 0.05 mg/L, As 10 mg/L, and Fe 500 mg/L. Figure 3, in conjunction with Table 3 demonstrates how MSF treats these interferences. For the typical processing technique (Area) without correction, the results are too high in all cases by a factor of 1.5 – 2. For MSF processing, all three lines generate the spiked concentration value more accurately.

Post-Analysis Spectra Viewing and Modification of Processing Parameters Followed by Reprocessing

In unknown environmental samples, it may happen that unexpected spectral interferences can be observed. As an example, this would be observed in wastewater after a problem in production had happened and an element normally not present might appear in the monitored effluent. This element could cause an interference on the analyte line (yielding too high a measured concentration) or an interference on a background correction point (yielding too low a concentration). In order to safeguard for this event, all spectra generated during an analysis run can be stored for post-analysis review. Observed interferences can be compensated for by modifying the processing parameters (e.g., adjusting background correction points or altering the processing technique such as changing to MSF).

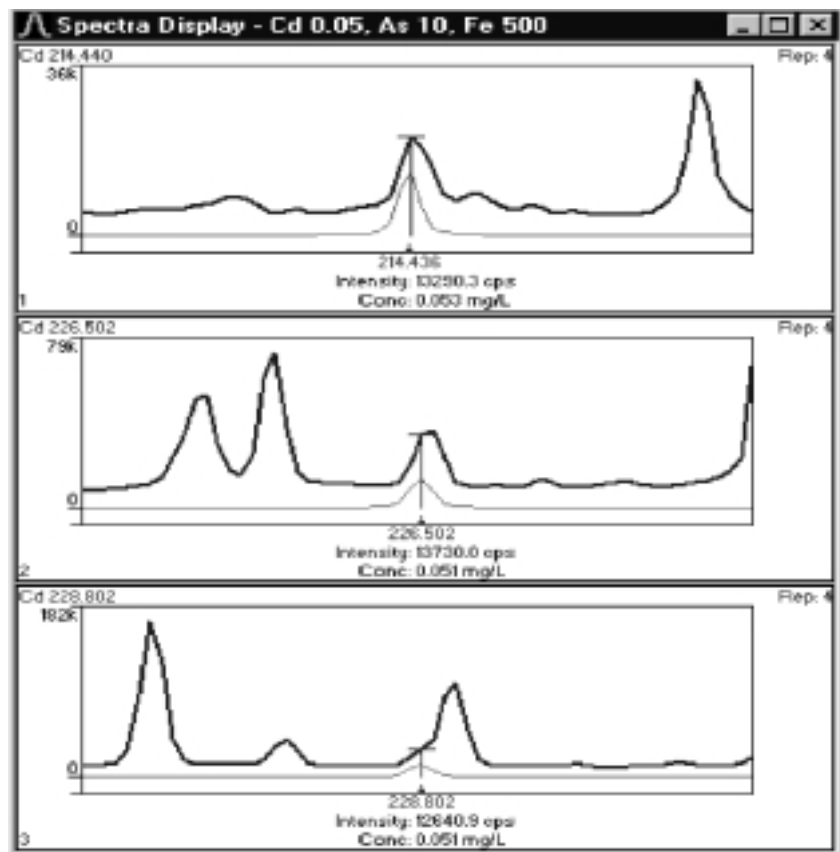


Figure 3: Spectral representation of the MSF processing for the determination of Cd 50 µg/L at its three principal lines in the presence of As 10 mg/L and Fe 500 mg/L. In each spectrum, the upper part represents the spectrum as generated by the sample, while the lower spectrum represents the fitted spectrum of the analyte Cd. The cursor represents the anticipated Cd peak position.

Table 3: Results for the Determination of Cd 0.05 mg/L in the Presence of Interferences

	Area	MSF
Cd 214.440	0.073	0.053
Cd 226.502	0.107	0.051
Cd 228.802	0.106	0.051

Analytical Results

In order to establish the system performance, a series of wastewater samples and sludge digests were measured along with selected certified standard reference materials.

Since the comparison of the measured concentrations vs. the certificate values for the reference materials can help evaluate the accuracy, only the measurements for the reference materials are reported.

Wastewater

The method and instrument performance was verified using reference material CWW-TM-G (Trace Metals in Certified Wastewater from High-Purity Standards, Charleston, SC, USA). The accuracy was calculated as the difference between measured and certified concentration, normalized to the certified concentration (expressed in %). The results are presented in Table 4. The accuracy and precision are considered very good for this type of environmental analysis.

Sludges

Two certified reference materials were used to check the accuracy of the method developed: BCR 145 (Trace Elements in Sewage Sludge from Community Bureau of Reference, Brussels, Belgium) and BCR 146 (Trace Elements in Sewage Sludge of Mainly Industrial Origin). The certified values correspond to aqua regia-leachable content, except for Hg, which is total content. There are no certified values for As, Ba, Be, and V. In order to have an estimate of the influence of the digestion (better extraction) procedure with aqua regia, the results for both digests are reported in Tables 5 and 6.

In general, the agreement between measured and certified concentrations is very good, except for Hg, which has consistently high results. These are reproduced from one digest to the next. Even though the results are high, they fall into a range of $\pm 20\%$, which is generally considered to be acceptable for this type of analysis. In the past, Hg was not considered to be an element determined by ICP-OES. With a suitable digestion procedure to retain mercury and if it meets the data quality objectives of the analysis (precision and accuracy), Hg can successfully be included in a multielement run. It is also useful

Table 4: Results for Certified Standard Reference Material Wastewater CWW-TM-G

Element	C (meas) (mg/L)	SD (mg/L)	RSD (%)	C (cert) (mg/L)	Accuracy (%)
Al	1.047	0.005	0.51	1.00	4.7
As	0.258	.006	2.2	0.25	3.2
Ba	0.0241	0.0001	0.52	0.025	-3.6
Cd	0.255	0.004	1.4	0.25	2.0
Co	1.036	0.002	0.23	1.00	3.6
Cr	0.0249	0.00005	0.20	0.025	-0.4
Cu	0.0250	0.0005	1.8	0.025	0.0
Fe	1.019	0.006	0.56	1.00	1.9
Mn	1.035	0.003	0.29	1.00	3.5
Mo	0.980	0.004	0.38	1.00	-2.0
Ni	0.259	0.001	0.29	0.25	3.6
Pb	0.0252	0.0001	0.40	0.025	0.8
V	1.00	0.007	0.71	1.00	0.0
Zn	0.0249	0.0003	1.2	0.025	-0.4

to include Hg for screening purposes. The measurement can then be used directly if a very high concentration is found and contamination of a dedicated mercury analysis avoided.

In all cases, the repeatability between replicate digested samples is much poorer than between instrument measurements on the same sample, indicating that the error of digestion process is higher than that of the measurement by the spectrometer. The reproducibility of the measurement is generally well below 1%, if the concentration is a comfortable margin above the detection limit. This is noteworthy, because the analysis was performed in aqua regia, which typically degrades precision.

Detection Limits

Since a number of elements in environmental samples can be present in very low concentrations, the limits of detection (LOD) were measured using the blank procedure. Ten replicates of the blank were measured as sample and the standard deviation was calculated from this. The measurement was repeated five times. The previously calculated standard deviations were averaged. The statistical factor was set at $k = 3$ (3σ). All numbers were rounded to one digit.

The detection limits calculated in solution (see Table 7) and in the solid (see Table 8) are low enough in many cases, even to measure drinking water levels, and are quite comfortable for wastewaters and sludges. By extending the read time, they can be further lowered.

Table 5: Results for Certified Standard Reference Material of Sewage Sludge BCR 145

Element	Digest 1 C (meas) (mg/kg)	SD (mg/kg)	Digest 2 C (meas) (mg/kg)	SD (mg/kg)	CRM C (cert) (mg/kg)	Confidence Interval
As	3.5	0.2	3.1	0.2	-	-
Ba	295	3	332	2	-	-
Be	0.203	0.001	0.201	0.002	-	-
Cd	17.7	0.1	17.4	0.1	16.8	1.6
Co	7.7	0.1	7.09	0.02	6.8	1.0
Cr	76.2	0.2	79	1	85.2	16.3
Cu	403	1	401	1	415.9	23.5
Hg	10.65	0.08	10.43	0.06	8.82	0.88
Ni	38.6	0.1	39.0	0.2	38.5	3.6
Pb	364	0.5	350	1	332	22
V	13.5	0.1	13.5	0.1	-	-
Zn	2835	5	2799	11	2772	209

Table 6: Results for Certified Standard Reference Material of Sewage Sludge BCR 146

Element	Digest 1 C (meas) (mg/kg)	SD (mg/kg)	Digest 2 C (meas) (mg/kg)	SD (mg/kg)	CRM C (cert) (mg/kg)	Confidence Interval
As	2.1	0.1	1.9	0.2	-	-
Ba	279	2	256	2	-	-
Be	0.322	0.005	0.3180	0.0003	-	-
Cd	76.5	1.1	76.8	0.7	76.5	4.9
Co	10.5	0.1	10.5	0.1	9.9	0.8
Cr	706	1	710	6	769	79
Cu	924	6	927	3	921	47
Hg	11.0	0.1	10.9	0.07	9.49	0.76
Ni	261	1	260	1	269	17
Pb	1330	7	1290	4	1255	41
V	22.9	0.2	23.3	0.2	-	-
Zn	3647	6	3649	8	4002	296

Table 7: Detection limits (3s) in aqua regia, expressed in µg/L

	LOD (µg/L) for a read time of:		
	1 s	5 s	20 s
As 197.197	20	5	4
Ba 233.527	0.7	0.3	0.4
Be 313.107	0.07	0.05	0.04
Cd 228.802	0.9	0.5	0.5
Co 228.616	1	0.5	0.2
Cr 267.716	1	0.5	0.4
Cu 327.393	2	0.8	0.5
Hg 194.168	6	2	1
Ni 231.604	2	1	1
Pb 220.353	6	3	2
V 292.464	1	0.7	0.7
Zn 206.200	1	0.4	0.2

Table 8: Detection limits (3s) in aqua regia, expressed in mg/kg

	LOD (µg/L) for a read time of:		
	1 s	5 s	20 s
As 197.197	0.7	0.2	0.1
Ba 233.527	0.02	0.01	0.01
Be 313.107	0.002	0.001	0.001
Cd 228.802	0.03	0.02	0.02
Co 228.616	0.04	0.02	0.01
Cr 267.716	0.04	0.02	0.01
Cu 327.393	0.05	0.03	0.02
Hg 194.168	0.2	0.08	0.04
Ni 231.604	0.06	0.04	0.03
Pb 220.353	0.2	0.09	0.08
V 292.464	0.04	0.02	0.02
Zn 206.200	0.03	0.01	0.006

Warm-up

For applications that are only run occasionally but require a rapid response time, the warm-up of the system was determined in a solution containing a simulated wastewater matrix. The solution contained 100 µg/L of the analytes and the following matrix elements: Al 100 mg/L, Ca 200 mg/L, Fe 400

mg/L, K 20 mg/L, Mg 10 mg/L, and Na 1 g/L. The warm-up function is displayed graphically in Figure 4. Within an error margin of 5%, most elements can be measured right after the plasma has been ignited, while Ba, Cd, Pb, and Zn require a delay of approx. 7 min to bring the error down to less than 5%. It should be noted that additional two

minutes are required for the computer-controlled plasma ignition routine and, in the case that the power had been turned off, another two minutes are needed for the initialization of the hardware components of the spectrometer. In the case that the instrument is started after a complete shutdown, the total time before quality data can be collected is 4 – 11 minutes.

Long-Term Stability

For the routine laboratory, it is important to spend as much of the up-time of the instrument for running samples rather than for calibration or recalibration. Therefore, the long-term stability is important as performance criteria. Figure 5 displays the results of an 8-hour run, measured for a solution containing a simulated wastewater matrix. In this concentrated matrix, the calibration was stable within ±5% of the initial calibration for eight hours for most elements.

The validity of the calibration can be monitored by a quality control module that is part of the application software. The user can insert quality control standards at selected intervals between the samples in an unattended automatic routine analysis run. If a user-defined concentration range is exceeded, a number of actions to maintain the validity of the calibration can be selected.

Conclusions

The scanning array ICP emission spectrometer studied has the analytical capabilities to analyze with good accuracy, precision, analysis speed, and robustness and fulfills the requirements normally set for the analysis of wastewaters and sludges. The rapid start-up from a shut-down state allows economical use of the instrument that is not limited by the requirements of rapid response. Long-term stability ensures that the calibration will be maintained during a long run, requiring fewer QC actions and possible reruns.

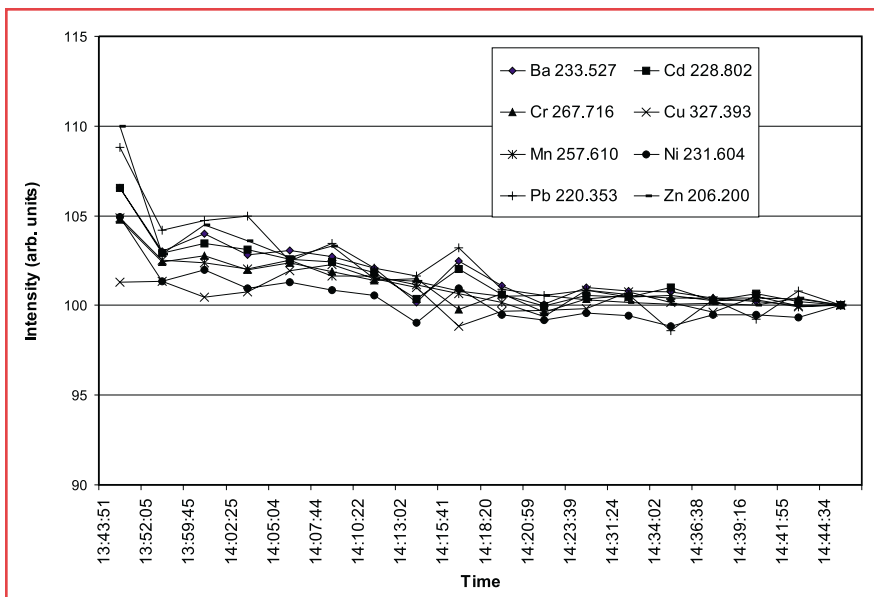


Figure 4: Warm-up of the Optima 2000 aspirating a simulated wastewater matrix normalized to the end of the warm-up period.

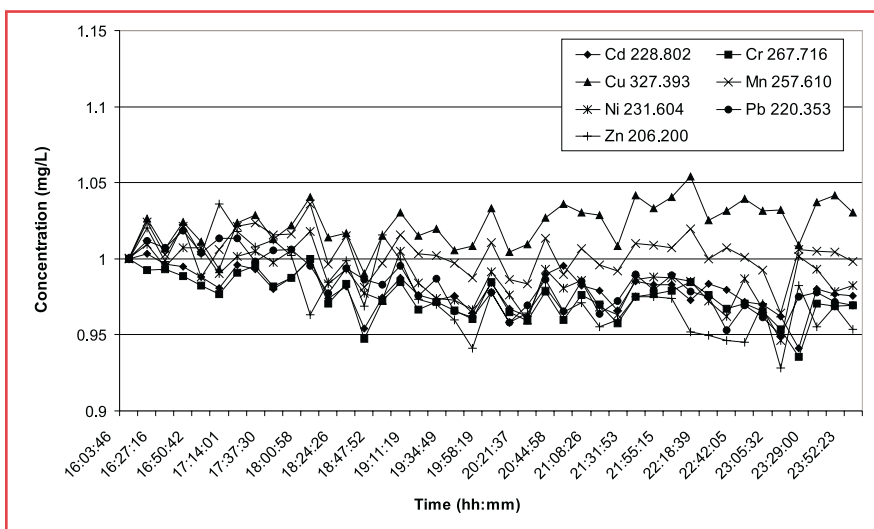


Figure 5: Long-term stability of the Optima 2000 in a simulated wastewater matrix.

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