Application Note · PlasmaQuant 9100

Challenge

Analysis of trace elements and precise determination of minor and major impurities in wastewaters

Solution

High-resolution ICP-OES with its DualView Plus option provides an extended linear dynamic range from sub-ppb level to %-range

Wastewater Analysis Following U.S. EPA 200.7 Using HR ICP-OES

Introduction

The analysis of wastewater for metal contamination is important to protect the environment and human health from harmful effects caused by insufficiently treated municipal wastewaters and from certain industrial discharges. However, wastewater is regulated differently in different countries. In the U.S., the Environmental Protection Agency (EPA), in conjunction with the states, negotiates a discharge permit through the National Pollutant Discharge Elimination System (NPDES). Federal guidelines for the industrial category (40 CFR, Parts 405-471)^[1] and the sensitivity of the waterway receiving the discharge are taken into account for each site.

The treatment of wastewater in the European Union is regulated in the Urban Wastewater Treatment Directive (UWTD) and Integrated Pollution and Control (IPC) Directive, both under the EU Water Framework Directive (WFD). The German wastewater regulation (Abwasserverordnung – AbwV) incorporates various EU directives concerning discharge limits for pollutants to reduce environmental

pollution. Unlike wastewater discharge regulations required by the Clean Water Act (CWA) in the U.S., the German Abwasserverordnung (AbwV) does not differentiate between direct and indirect discharge. Both have to comply with the requirements for the individual industry or communal wastewater. Therefore, wastewater may need to be measured for a variety of metals at varying concentrations, in different water matrices.

There are several inorganic techniques which can be used to measure the elemental composition of wastewaters. This includes atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and ICP mass spectrometry (ICP-MS). Depending upon the number of elements and samples, the most suitable technique for each application's requirements can be chosen. Whereas ICP-MS provides highly accurate trace detection capabilities, it is not well suited for determining mineral contents of 200 mg/L with high accuracy and precision. Common ICP-OES instrumentation provides far better

performance for the assessment of mineral and pollutant contents but often lacks the sensitivity to reliably detect toxic trace metals. The application itself is described in several ICP-OES standard procedures such as US-EPA Method 200.7[2] or ISO 11885[3]. The U.S. EPA developed Method 200.7 for the determination of metals and trace elements in waters and waste by ICP-OES. The method itself is applied to a variety of sample types but is used extensively for wastewater applications. The method includes a quality control program to ensure proper instrument and methodology operation during the analysis of wastewater samples.

Within this study, the performance of the PlasmaQuant 9100 Elite ICP-OES, featuring high sensitivity, a wide linear dynamic range, and a high spectral resolution, was evaluated for the analysis of wastewater. The here presented approach describes the analysis of pollutants and trace elements in wastewater with a standard ICP-OES setup. The suitability of this methodology was validated by performing a quality control program in accordance to Method 200.7, analyzing several certified reference materials, participating in a national round robin test for external quality control, checking for spike recoveries in challenging matrices, and monitoring the system's long-term stability.

Materials and Methods

Sample preparation

All laboratory ware was washed with deionized (DI) water from a PURELAB system (18.2 MΩ cm, ELGA LabWater, High Wycombe, England). The single and multi-element working standards were prepared by serial volume/volume dilution in polypropylene tubes from the stock solutions (Merck, Sigma-Aldrich, CPAChem, Inorganic Ventures) using 1% (v/v) subboiled distilled HNO₂. All samples (if not already stabilized) and blank solutions were acidified with HNO₃ to give a final acid concentration of 1% (v/v). Yttrium (Y) was added on-line to all blanks, standards, and samples as internal standard.

This study also included several types of water (surface and ground water) and wastewater samples as well as the reference materials used for validating the developed method, which are summarized in Table 1. Additionally, three wastewater samples analyzed were part of a national round robin test (RRT) ("59th National Round Robin Test - Elements in Wastewater - 03/21" from the Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft Sachsen(BfUL), Germany). All samples were acidified with subboiled HNO₂ to give a final acid concentration of 1% (v/v) except for the RRT samples.

The sample preparation for the RRT samples was performed in accordance to EPA Method 3015A (SW-846)^[4] and DIN EN ISO 15587-2[5], which requires a microwave-assisted acid digestion step. Therefore, a 25.0 (\pm 0.1) mL aliguot of the sample and 6.25 (\pm 0.10) mL subboiled HNO₃ were added to a digestion vessel (PM60). The mixture was swirled

carefully and left standing for at least 15 minutes before the vessel was closed. Subsequent heating (20 min, 200 °C) was performed in a speedwave XPERT microwave digestion system. Afterwards the vessels were allowed to cool to room temperature (RT) to avoid foaming and splashing. The solutions were transferred to a graduated polypropylene tube and diluted to 50 mL with DI water. In the case of mercury (Hg), the sample preparation of the RRT samples was modified to fully comply with DIN EN ISO 12846: 2012-08 (E12). The samples arrived already stabilized (1 mL conc. HCl per 100 mL) and were stored only in glass containers over the whole procedure. 25 (± 0.1) mL of each sample were added to a 50 mL glass vial, combined with 0.5 mL of a 1:1 solution of potassium bromide (c (KBr) = 0.2 mol/L) and potassium bromate (c $(KBrO₃) = 0.033$ mol/L), and incubated (24 h, RT). After the incubation, 10 µL of a hydroxylammonium chloride $(\beta$ (NH_aOCl) = 120 g/L) and 0.5 mL of subboiled HCl were added to the reaction mixture, which was analyzed immediately afterwards. Blank and standard solutions were prepared accordingly. The determination of Hg is based on a cold vapor approach. The reducing agent consisted of 3.0 g sodium borohydride (NaBH $_{a}$) and 1 g sodium hydroxide (NaOH) dissolved in 1 L DI water, which corresponds to a concentration of 0.3% (m/v) and 0.1% (m/v), respectively. Samples were diluted 10-fold with 5%(v/v) subboiled HCl and analyzed.

Table 1: List of samples and reference materials being analyzed

Calibration

Calibration levels for each element were chosen based on expected concentration range. At least three calibration standards were used for each element, as described in Table 2. Selected calibration curves are shown in Figure 1.

Table 2: Concentration of calibration standards

Figure 1: Selected calibration functions

Instrument Settings

The analysis was performed on a PlasmaQuant 9100 Elite ICP-OES. The sample introduction components as well as the instrumental settings were selected to achieve a high level of sensitivity for trace elements in possibly high-salt containing matrices. In conjunction with this instrument, a Teledyne CETAC ASX-560 autosampler was used. An internal standard mixing kit was also used to introduce a 10 mg/L yttrium internal standard solution online, resulting in approx. 1 mg/L final concentration. A summary of individual settings and components is given in Table 3.

Table 3: List of samples and reference materials being analyzed

Method and Evaluation Parameters

Table 4: Method parameters

Table 4 (continued): Method parameters

1 **A**utomated **B**aseline **C**orrection

Results and Discussion

The EPA method 200.7 requires a formal quality control (QC) program. This program includes at minimum the initial demonstration of laboratory capability and the ongoing analysis of blanks and other laboratory standards to ensure the instrument's performance.

The initial demonstration of laboratory capability is comprised of the determination of method detection limits (MDLs) and linear dynamic range (LDR), periodically checks of blank solutions, as well as instrument performance (IPC) and spectral interference checks (SIC). Additionally, the accuracy and long-term stability of the method needs to be tested.

Linear dynamic range and method detection limits

According to Method 200.7, the LDR is defined as the upper limit which recovers within 10% of the actual value when determined against the calibration curve used for the analysis. The MDLs are determined from seven measurements of a blank solution which has been spiked at a concentration of two to three times the instrument detection limit. The resulting standard deviation of the seven measurements is then multiplied by 3.14 (at 99% confidence level) to give the MDL. The method specific LDRs and MDLs are shown in Table 5.

Table 5: Method detection limits (MDL) and upper limit of the linear dynamic range (LDR) for analytical lines utilized

* upper limit of test, even higher concentrations are possible by fulfilling the 90% recovery criteria

Laboratory reagent blank (LRB) and laboratory fortified blank (LFB)

Method 200.7 requires periodic measurements of different blank solutions. One of them is the laboratory reagent blank (LRB) which is processed in the same way as samples containing all reagents in the same volumes. It should be analyzed with each batch of 20 or fewer samples (same matrix) to address possible contamination from the laboratory environment and should not exceed 10% of the analyte levels determined or should be smaller than 2.2 times of the MDL. The other blank is the laboratory fortified blank (LFB) which is prepared by spiking an aliquot of LRB with a suitable analyte concentration. The LFB also must be carried through the whole sample preparation and should be analyzed with each batch of samples. The accuracy, calculated as percent recovery, has to be within a $\pm 15\%$ control limit. All LRBs and LFBs were prepared and analyzed in accordance to Method 200.7 and fulfilled all criteria.

Quality control sample, instrument performance check and stability

Directly after the calibration two different QC samples must be run to verify the quality of calibration standards and instrument performance. This includes the quality control sample (QCS) and the initial performance check (IPC) solution. The IPC should originate from the same source, while the QCS should be made from a different stock solution. The recovery of both standards must be within ±5% of the stated value. The specific standards were spiked at 0.01 mg/L (Hg), 0.5 mg/L (majority of elements), 5 mg/L (Mg, P, Si), and 50 mg/L (Ca, K, Na), respectively. All elements fulfill the criterion as indicated in Figure 2.

Additionally, the quality program requires the continuous measurement (every ten analyses and at the end of the run) of the IPC over the entire period of the analytical sequence. The ongoing IPC results were consistently within the allowed range of 90-110% of the known value, as shown in Figure 3. Figure 4 shows the behavior of the internal standard yttrium in axial and radial observational view. Relative standard deviations below 1.55% indicate a highly stable performance of the instrumentation throughout the 14 hours measurement.

Figure 3: Percentage recoveries in the IPC solutions throughout a 14-hour sequence. RSD values were below 1.65% for all elements

Figure 4: Percentage recoveries of the internal standard (yttrium) throughout a 14-hour sequence. RSD values were below 1.55% for both observational views.

Spectral interference check

As part of the QC program, a spectral interference check (SIC) solution has to be tested periodically to verify the interelemental spectral correction routine. For those instruments which do not use interelement corrections (IEC), SIC solutions (containing similar concentrations of major components in sample, e.g., ≥ 10 mg/L) can serve to verify the absence of spectral interferences at the selected analytical lines. Since the PlasmaQuant 9100 Elite employs a high-resolution optical system (2 pm @ 200 nm), the accessibility of the most common elemental lines is guaranteed and therefore makes IEC tools obsolete. Nevertheless, a SIC solution containing 200 mg/L Al and 300 mg/l Fe was analyzed and showed no significant interferences for the selected wavelengths.

Assessing analyte recovery

Since the chemical nature of the sample matrix affects the analyte recovery, Method 200.7 requires for spiking experiments in at least 10% of the routine samples before sample preparation. The recovery of the spiked analyte concentration must be within ±30% of the concentration equivalent added to the sample. To address this, high solid wastewater samples originating from the automobile and galvanic industry were spiked before the sample preparation with 0.5 mg/L of the desired elements. Figure 5 shows the analyte recoveries which all were within a $\pm 20\%$ range illustrating the applicability of the analytical method.

before microwave digestion following EPA Method 3015A (SW-846) and DIN EN ISO 15587-2.

Additionally, reference materials can be analyzed to demonstrate the validity of a method. Therefore, four wastewater reference materials were analyzed. Table 6 shows the certified values and recovery rates for the tested reference materials. All recoveries were within ±10% of the certified value. In addition, a wastewater reference material was analyzed containing low concentrations (close or below the legal limits of important drinking water regulations) of arsenic (As), mercury (Hg) and selenium (Se). The recovery rates were within ±14% for these elements indicating the applicability of the method for critical elements, such as As and Hg, even in the lower concentration range that is close or below legal limits by using a standard sample introduction kit.

Table 6: Quantitative results for several certified reference materials (CRMs)

Table 6 (continued): Quantitative results for several certified reference materials (CRMs)

Table 7: Quantitative results for certified reference material WW CA 713

External quality control – Round robin test

A round robin (or proficiency) test (RRT) is a method of external quality assurance for different measurement procedures. Basically, identical samples are tested with identical or with different procedures in multiple laboratories. The comparison of the results allows statements to be made about the measurement accuracy in general or about the measurement quality of the participating laboratory.

To demonstrate the PlasmaQuant 9100's performance and the applicability of the analytical method, the application lab of Analytik Jena's headquarter took part in a national round robin test. This test included the analysis of three wastewater samples. The sample preparation was carried out as described in the "Samples and Reagents" section. The organizer of the RRT specified the approved analytical methods and the corresponding regulations for sample preparation.

Table 8: Quantitative results for round robin test samples

^a calculation of z-score was performed in accordance to DIN 38402-45:2014-06

b determined by using cold vapor ICP-OES

The concentration of Hg in the RRT samples was determined by using cold vapor ICP-OES. Therefore, the PQ 9100 Elite was equipped with the hydride generation system HS PQ Pro (see Figure 6). With the addition of this system, the unique sensitivity of HR-Array ICP-OES PlasmaQuant 9100 Elite could be further improved achieving detection limits lower than 10 ng/L for Hg.

Figure 6: Calibration curve for the analytical line of Hg at 184 nm using cold vapor ICP-OES (left). On the right, the HS PQ Pro is shown in the sample chamber of the PQ 9100 Elite.

Conclusion

The here presented method describes the use of a highresolution ICP-OES in a standard configuration by fully complying with the requirements of EPA Method 200.7 for a wide range of wastewater samples. It was demonstrated that the PlasmaQuant 9100 Elite successfully follows the strict quality control requirements of the method by providing excellent sensitivity, accuracy, and long-term stability. Additionally, the instrument's performance and the applicability of the analytical method was successfully confirmed by passing a national round robin test. The major challenge of this application includes analyzing elements over a large concentration range (low μg/L to high mg/L) in a single run. Trace elements (e.g., As, Hg) are to be analyzed together with high-concentrated minerals (e.g., Mg, Na) and pollutants (e.g., Al, Fe), which is successfully addressed by the DualView Plus feature of the PlasmaQuant 9100 Elite. Besides the common radial and axial plasma observation modes it offers, axial plus and radial plus views, which attenuate the signal in the respective observation mode, are available. The here described method uses radial plasma observation to measure the high levels of minerals alongside the axial view for trace levels of toxic elements in a single measurement run. Running several dilutions to cover the entire concentration range is therefore avoided.

The method validation included the accuracy determination on CRMs and several spiked wastewater samples demonstrating the suitability of the PlasmaQuant 9100 Elite ICP-OES system to comply with wastewater as well as even drinking water directives, such as the Safe Drinking Water Act, the European Drinking Water Directive, or the German drinking water ordinance. A typical issue with ICP-OES instrumentation is the lack of sensitivity to meet the regulations for trace element detection. In this regard, the PlasmaQuant 9100 Elite offers a high sensitivity which is based on a multitude of technical features. The high frequency generator provides a plasma with superior robustness to deliver a strong and constant signal intensity, even for wastewater samples with high salt contents. The four-wind coil in combination with the counter gas technology provides an elongated analytical zone in axial observation mode to provide as much signal as possible in ICP-OES. On top of this, the spectral resolution of 2 pm @ 200 nm (Figure 7) makes the use of laborious correction algorithms, such as inter-element, correction obsolete. This allows for a reliable and interference-free quantification of trace elements by granting access to most sensitive emission lines and high-definition peak shapes with extra sensitivity.

Figure 7: PlasmaQuant 9100 Elite and PlasmaQuant 9100

The here proposed setup fulfills all requirements for water and wastewater quality monitoring. The use of the PlasmaQuant 9100 Elite allows water laboratories to perform their entire elemental screening on one instrument by using a standard sample introduction kit to save costs, lab space, time and labor. The performance can be even further improved by using a hydride system to push the method detection limits of mercury and hydride forming elements into the ng/L range.

References

- [1] 40 CFR, Parts 405-471, U.S. Code of Federal Regulations
- [2] EPA Method 200.7, "Determination of Metals and Trace Metals in Water and Wastes by Inductively Coupled Plasma Atomic Emission Spectrometry", Rev. 4.4
- [3] ISO 11885, "Water quality Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)"
- [4] EPA Method 3015A (SW-846), "Microwave Assisted Acid Digestion of Aqueous Samples and Extracts"
- [5] DIN EN ISO 15587-2:2002, Wasserbeschaffenheit Aufschluss für die Bestimmung ausgewählter Elemente in Wasser Teil 2: Salpetersäure-Aufschluss; Deutsche Fassung

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