Challenge

Standard-compliant determination of various parameters including anions (group D), cations (group E) and substance group analysis (group F) in wastewater.

Solution

Spectrophotometric determination of nitrate (NO_3), nitrite (NO_2), ammonium (NH_4) and phosphate (PO_4) ions and total phosphor (P_{tot}) in wastewater using the SPECORD 50 PLUS.

Spectrophotometric Determination of Standard Parameters in Wastewater According to Standard Methods

Introduction

In July 2010, the United Nations General Assembly declared the access to clean water and sanitation to be a human right.[1] This emphasizes the significance of clean drinking water as one of the most vital resources with ever increasing importance. To ensure future access to this vital resource, it is essential to effectively purify polluted wastewater. One important step for the purification procedure is the precise qualitative and quantitative analysis of the pollutants.

Among other impurities, total phosphorus (P_{tot}), phosphate (PO_4), ammonium (NH_4), nitrate (NO_3) and nitrite (NO_2) ions are not only present in industrial and household wastewater in varying concentrations, but are also found in drinking water, ground water, and surface water. The first step in the purification procedure of wastewater in sewage treatment plants is the removal of solids with physical methods. Bacterial and yeast oxidation processes occur in the following biological stage. The mainly organically bound nitrogen (as proteins, nucleic acids, and urea) is then oxidized to NO_3 and NO_2. During the third step, the chemical purification, PO_4 is precipitated.

The spectrophotometric determination of the above mentioned compounds is regulated in the German standard methods for examination of water, wastewater and sludge (DIN 38405) and other standards.[2,3] Detailed instructions for the analysis including sample preparation, interfering ions, as well as detection limits are given. The SPECORD 50 PLUS spectrophotometer with its high-resolution optics and robust construction ensures precise and reliable data acquisition. The software ASpect UV supports fast and standard-compliant measurements and data evaluation through the straightforward method for the creation of calibration curves. The use of accessories for large sample throughput, such as the cell carousel with 15 positions and the 6-fold cell changer, additionally supports the simple and fast handling of large sample quantities.

Materials and Methods

Instrumentation and software settings

All measurements were performed using a SPECORD 50 PLUS spectrophotometer equipped with the 15-position cell carousel for the analysis of NH_4, NO_2, and NO_3 or the 6-fold cell changer for the analysis of PO_4 and 10 mm glass cuvettes. Using the ASpect UV software 1.4.4 (other versions of ASpect UV give the same results), the absorbance for each parameter was measured at one defined wavelength. The software settings are shown in Table 1.

Table 1: Software settings.

	NH_4	**NO_2**	**NO_3**	**PO_4**
Measurement mode	Absorbance	Absorbance	Absorbance	Absorbance
Wavelength [nm]	655	540	338	880
Integration time [s]	0.2	0.2	0.2	0.2
Regression	y = B*x	y = B*x	y = B*x	y = B*x

The measurement settings were made using the photometry module of the software ASpect UV. Required evaluations can be set in the method. Concomitantly, a report in PDF format can be saved directly after the measurement. The set and saved method for each parameter was stored in the Quick Start menu.

Samples and reagents

Standard and sample preparation were carried out according to the DIN standards[3]. The conditions for the calibration curves according to standards are shown in Table 2.

Measurement

The prepared samples were measured within the following times:

- NH_4: 1–3 h
- NO_3: 1 h
- NO_2: 20 min
- PO_4 / P_{tot}: 10–30 min

Reference, blank and samples were measured sequentially. The reference was measured against air. For the blank distilled water was used and identically prepared as the wastewater samples. The absorbance of the blank was automatically subtracted from the subsequent samples.

Results and Discussion

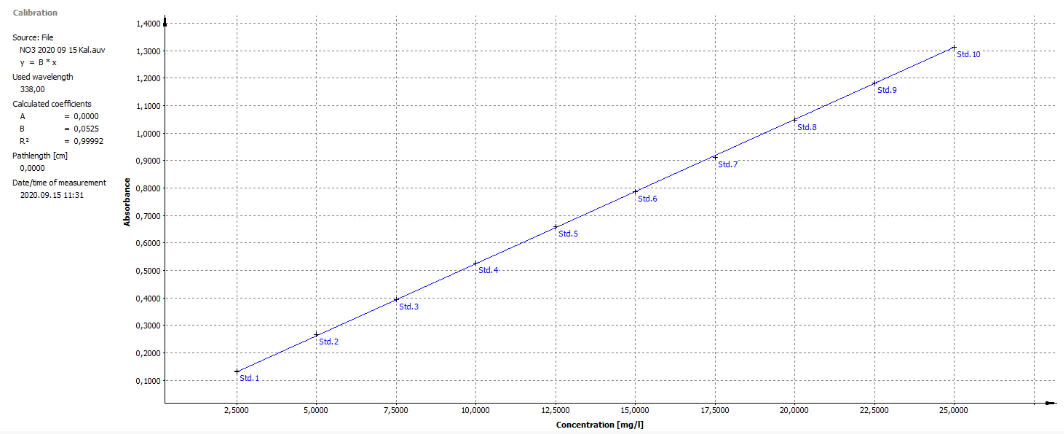
Creation of calibration curves

To determine the concentration of NH_4, NO_3, NO_2, PO_4 and P_{tot}, the first step is the creation of the calibration curve according to the referenced standards.[3] According to literature, ten distinct solutions with varying reference concentration were prepared. Table 2 shows the preparation conditions for the calibration standards and subsequent plotting of calibration curves for each parameter according to the referenced standards.

Table 2: Conditions for the creation of calibration curves according to standards.

Standard	Parameter	Concentration range	Reference compound	Wavelength
DIN 38406-05	NH_4	0.03–1 mg/L	Ammonium sulfate ($(NH_4)_2SO_4$)	655 nm
DIN 38405-9	NO_3	0.5–25.0 mg/L	Potassium nitrate (KNO_3)	338 nm
DIN EN 26777	NO_2	up to 0.25 mg/L	Sodium nitrite ($NaNO_2$)	540 nm
DIN EN ISO 6878	PO_4 / P_{tot}	0.005–0.8 mg/L	Potassium dihydrogen phosphate (KH_2PO_4)	880 nm

As an example, the calibration curve of NO_3 is shown in Figure 1. The absorbance of the blank measurement with distilled water is automatically subtracted in the ASpect UV software from the absorbances of the standard measurements. The calculated absorbance of the standard solutions is plotted as a function (y-axis) of the standard solution concentration (x-axis). The later one is given in milligrams per liter (mg/L). As observed in Figure 1, correlation between the absorbance and the concentration within the given ranges, clearly indicates a linear dependency. The ASpect UV software automatically calculates the slope and R²-value of the calibration curve. The unknown concentration of any sample is then automatically derived upon absorbance measurement. In addition, the concentration is also automatically calculated if information about dilution and initial weight (initweight) of the sample is given. Therefore, calculation errors can be excluded, and the user saves valuable analysis times.



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Calibration

Source: File
  NO3 2020 09 15 Kal.auv
  y  =  B * x
Used wavelength
  338,00
Calculated coefficients
  A            =  0,0000
  B            =  0,0525
  R²           =  0,99992
Pathlength [cm]
  0,0000
Date/time of measurement
  2020.09.15 11:31
```

Figure 1: Calibration curve for the determination of concentration of NO_3.

Measurements of wastewater samples

It is important to note that the impact of other substances on the absorbance needs to be verified prior to estimating any parameter result, as interfering ions (e.g., NO_3 and NO_2: chlorid; PO_4: arsenat) can significantly affect the test results. If the presence of interfering ions can be excluded, the wastewater samples are treated with the detection reagents as described in the standards. Subsequently, the absorbance of the wastewater samples is measured, and the concentration is determined using the calibration curve. If the selected parameters are frequently measured, it is recommended to save the methods and calibration curves in the Quick Start function (see Figure 2). This enables fast and precise measurement as well as rapid evaluation of further samples. After opening the software ASpect UV, the method starts and the results are automatically recorded and evaluated within just four clicks (sample sequence including number of samples and sample names can additionally be adjusted). Five water samples had been measured after the purification procedure. The results are shown in Table 3. Due to the continuous monitoring of the concentration of different parameters, the purification process of wastewater in the sewage plants can be reviewed. The measurement's data are recorded and stored for review of the authorities to check if the values are within the threshold. Additionally, a continuous improvement and optimization of the purification process can be achieved.

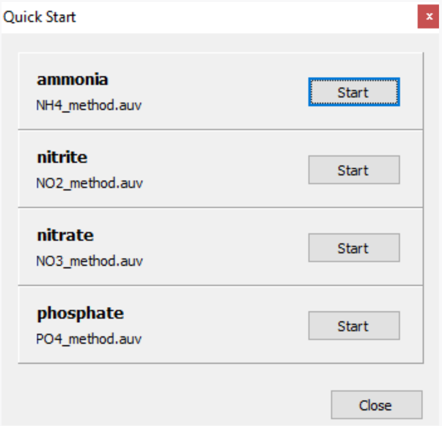

Figure 2: Quick Start menu of the ASpect UV software.

Table 3: Concentration of the selected parameters exemplified for five wastewater samples from a sewage treatment plant.

Sample	NH_4	NO_2	NO_3	P_{tot}	PO_4
1	0.5035	0.4839	12.2777	0.2066	-
2	0.0237	0.0079	5.8712	0.1991	0.0666
3	0.0813	0.0305	6.7569	0.2237	0.0724
4	0.0194	0.0157	5.0116	0.0246	-
5	0.0105	0.0139	3.8557	0.0267	-

Depending on the pH value, ammonia can be present in wastewaster samples in different forms (as ammonium ion (NH_4^+), ammonia (NH_3), or ammonium hydroxide (NH_4OH)). In order to detect all possible ammonia species and therefore get reliable results independently of the source and pH value of wastewater, severe alkaline conditions are required. Conversely, in order to catalyze the formation of the chromatic target compounds and thus alllowing detection at the characteristic wavelength, stronger acidic solutions for the detection of NO_3 and NO_2 ions are required.

Due to extreme conditions of the solutions, the handling of the samples is complicated. Additionally, the use of large quantities of solvent should be avoided in order to reduce the amount of hazardous waste. Therefore, the measurements are preferable performed in 10 mm cuvettes, although 40 mm or 50 mm cuvettes are also permitted according to the standards. Another advantage of the use of the 10 mm cuvettes over 40 mm or 50 mm cuvettes is a higher suitability for sample automation. Whereas 40 mm or 50 mm cuvettes can only be treated individually or in a 6-fold cell changer, the 10 mm cuvettes can additionally be placed in a 15-position carousel or an 8-fold cell changer. Further automation procedures can be established using the APG autosampler and sipper system.

The SPECORD PLUS spectrophotometers are particularly suitable for the analysis of wastewater samples, as a a special cuvette position for turbid samples is included. The cuvette can be closely positioned to the detector and therefore the amount of scattered light is reduced. The SPECORD 50 PLUS spectrophotometer with the split-beam-technology provides a high energy flux from the light sources, which is especially suitable for the analysis of highly concentrated wastewater samples. The use of standardized test kits for water analysis parameters such as SAC, turbidity, COD, BOD, sulfate, and many more is possible with the use of the round cuvette holder. Low concentrated samples can easily be analysed with the use of 100 mm cuvette holder to increase the path length.

Conclusion

The SPECORD 50 PLUS spectrophotometer allows fast, precise, and simple determination of the concentration of important water parameters in wastewater samples. The calibration curves can be created with good R^2-values, with the help of the high precision optics. The automatic calculation of the concentration depending on dilution and initial weight in the software ASpect UV supports the fast and error-free calculation of the concentration of different pollutants in the wastewater samples. The use of accessories such as the autosampler, cell changer, or cell carousel support high-throughput measurements. Additional equipment enables the analysis of turbid and low concentrated samples.

References

[1] United Nations – Water

[2] Verordnung über Anforderungen an das Einleiten von Abwasser in Gewässer (Abwasserverordnung - AbwV)

[3] DIN 38406-05:1983-10 (E5-1); DIN 38405-09:2011-09 (D9); DIN EN 26777:1993-04 (D10); DIN EN ISO 6878:2004-09 (D11, part 4); DIN EN ISO 6878:2004-09 (D11, part 7)

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Version 1.1 · Author: JuTy / SaWu
en · 06/2024