Supelco®
Analytical Products

Application Note

Cobalt in wastewater from printing plates, print materials, and graphic products

Photometric Determination with Nitroso-R-Salt

Introduction

Cobalt and cobalt compounds can occur in the wastewater during the production of printing plates, print materials, and graphic products, including the offset-printing and sieve-printing sectors [1].
Cobalt salts have a carcinogenic effect when absorbed by inhalation, and in the event of oral uptake have a health-hazardous effect after repeated exposure [2].
As a measure to prevent any impact on the environment and humans, the limit for the discharge of wastewater into water bodies imposed by Annex 56 of the German wastewater directive is set at 1 mg/l Co [1].
The concentration of cobalt in water bodies and wastewater can be measured using the Spectroquant® Cobalt Cell Test Cat. No. 1.17244. This test offers a swift and precise alternative to conventional spectrometric methods such as ICP-OES (ISO 11885:2009, DIN 38406-24:1993-03, US EPA 200.7) and ICP-MS (US EPA 200.8). [3, 4, 5, 6].

Experimental

This Application Note describes the determination of cobalt in wastewater from printing plates, print materials, and graphic products using the Spetroquant® Cobalt Cell Test Cat. No. 1.17244.

With the Spectroquant® Cobalt Cell Test the cobalt concentration in wastewater can be determined quickly and easily.
The methods are preprogrammed on the corresponding Spectroquant® photometers. Calibration is not necessary. All reagents required for the measurement are included in the test kit.
25 determinations can be carried out per package.

Method

Cobalt(II) ions react with Nitroso-R salt to form an orange-red complex that is determined photometrically.

Measuring range

0.05 – 2.00 mg/l Co

Sample material

Wastewater from the production of printing plates, print materials, and graphic products, including the offset-printing and sieve-printing sectors.

Reagents, Instruments and Materials:

Reagents

Cat. No. 1.17244 Spectroquant® Cobalt Cell Test
Cat. No. 1.09535 MQuant® Universal indicator strips pH 0–14

Only necessary, if:
Sample needs to be preserved:
Cat. No. 100456 Nitric acid 65 % for analysis

pH adjustment is needed:
Cat. No. 109137 Sodium hydroxide solution 1 mol/L Titripur®

Sample blank is needed:
Cat. No. 116754 Water for analysis EMSURE® or distilled water

Total cobalt should be determined:
Cat. No. 114688 Spectroquant® Crack Set 10C
Cat. No. 114687 Spectroquant® Crack Set 10
+ empty cells 16 mm with screw caps (Cat. No. 114724)

For analytical quality assurance:
Cat. No. 119785 Cobalt Standard 1000 mg/L Co CertiPur®

Instruments

For the cobalt measurement one of the following Spectroquant® photometers is necessary:
Cat. No. 1.73028 Spectroquant® UV/VIS Spectrophotometer Prove 600 plus
Cat. No. 1.73027 Spectroquant® UV/VIS Spectrophotometer Prove 300 plus
Cat. No. 1.73026 Spectroquant® VIS Spectrophotometer Prove 100 plus
Cat. No. 109752 Spectroquant® Photometer Nova 60A
Cat. No. 173632 Spectroquant® Colorimeter Move 100
Also first generation Prove instruments are compatible and preprogrammed with this method.

If total cobalt should be determined, one of the following thermoreactors is necessary:
Cat. No. 171200 Spectroquant® Thermoreactor 320
Cat. No. 171201 Spectroquant® Thermoreactor 420
Cat. No. 171202 Spectroquant® Thermoreactor 620

Software for data maintenance

The Spectroquant® Prove Connect to LIMS software package provides an easy way to transfer your data into a preexisting LIMS system. This software can be purchased under:
Cat. No. Y11086 Prove Connect to LIMS

MQuant® StripScan App

The MQuant® StripScan App is an analytical detection system for the readout of test strips. The app can be downloaded via the IOS app store (the app is currently available for iPhones only). In addition to the app a reference card is necessary which can be purchased under the below-mentioned Cat. No..
Cat. No. 103736 MQuant® StripScan Reference Card for the measurement of MQuant® pH-indicator strips pH 0 – 14

Materials

Pipettes for pipetting volumes of 0.50 and 5.0 ml

Only necessary for turbid solutions:
Filter, e.g. Syringe filter Millex-LCR Filter 0.45 µm, hydrophiles PTFE, Cat. No. SLCR025NS

Analytical approach

Sample preparation

- Analyze immediately after sampling. Otherwise preserve with nitric acid 65 % (1 ml nitric acid per 1 l of sample solution). After acidifying the sample is stable for 4 weeks, acc. to. EN ISO 5667-3:2012.
- The pH range must be within 2.5–7.5. Check the pH using MQuant® pH indicator strips in combination with the MQuant® StripScan App. Adjust, if necessary, with sodium hydroxide solution or nitric acid.
- Filter turbid samples.
- The test determines cobalt(II)-ions only. Undissolved or complex-bound cobalt or cobalt that is present in an organometallic compound can be determined after pretreatment of the sample using one of the Spectroquant® Crack Sets and a thermoreactor. Details on how to perform the digestion see product packaging insert of the corresponding Crack Set.

Preparing the measurement solutions[1)]

Sample blank (optional)
If the sample is colored, perform a sample blank before the measurement of the sample itself. This step is necessary to compensate for the intrinsic color of the wastewater.

The sample blank is prepared as followed:

- Pipette **5.0 ml of the pretreated sample** into a reaction cell, close the cell, and mix.
- Add **0.5 ml of water for analysis** or distilled water with a pipette, close the cell tightly, and mix. The pH should be approx. 4.8.
- **Leave to stand for 10 min (reaction time),** then measure the sample blank in the photometer.

Measurement sample

- Pipette **5.0 ml of the pretreated sample** into a reaction cell, close the cell, and mix.
- Add **0.5 ml of reagent CO-1K** with a pipette, close the cell tightly, and mix. The pH should be approx. 4.8.
- **Leave to stand for 10 min (reaction time),** then measure the sample in the photometer. The color of the measurement solution remains stable for at least 60 min after the end of the reaction time.

[1)] Due to the instrument design of the Move 100 there may be differences in preparing the reagents as well as performing the measurement. Please see the Move 100 Manual for details.

Measurement[2)]

- Insert the reaction cell into the measurement shaft, the method opens automatically.
- It is recommended to check the zero adjustment each new working day. To do this, open the cobalt method, activate the absorption measurement (at 500 nm) and insert a round cell filled with distilled water in the measurement compartment. If the absorption is > 0.005 Abs, re-zero photometer.
- If the sample is colored, perform a sample blank. Therefore, configure the photometer for sample blank measurement and insert the sample blank cell into the cell compartment. After measurement confirm with OK.
  Hint: On the Prove instruments the sample blank is valid for the next measurement only.
- Insert the cell with the measurement sample into the shaft. The measurement starts automatically.
- Read off the result in mg/l from the display.

[2)] For Details on how to perform the measurement step by step, see the instrument-specific manual

Data transfer Prove spectrophotometers

After measurement transfer the values measured on the Prove spectrophotometer using Prove Connect to LIMS.

Influences of foreign substances

The cobalt determination is interfered with by the presence of certain substances. For details see the packaging insert of the test kit.

Analytical Quality Assurance

The objective of analytical quality assurance (AQA) is to secure correct and precise measurement results. AQA is recommended before each measurement series. To check the measurement system (test reagents, measurement device, and handling) the ready-to-use cobalt standard solution Certipur®, concentration 1000 mg/l Co (Cat. No. 119785), can be used after diluting accordingly. Sample-dependent interferences (matrix effects) can be determined by means of standard addition.
For details on how to perform the AQA check see the instrument-specific manuals.

A certificate of analysis is provided for each batch and can be downloaded online on the product page of the test as well as a certificate of quality, where all batches are taken into account. In the certificates the performance characteristics determined in accordance with ISO 8466-2 and DIN 38402 A51 are given. Nevertheless, it is recommended to determine the performance characteristic yourself so that all specific factors that may impact the performance (test reagents, measurement device, handling) are considered in the characteristic data.

Conclusion

The Spectroquant® Cobalt Cell Test is a fast and cost-effective alternative to spectrometric methods such as ICP-OES and ICP-MS for the determination of cobalt in wastewater.
The method is preprogrammed on the corresponding Spectroquant® photometers, so there is no need for a time-consuming calibration.
Stringent controls of the raw materials, effective in-process controls and documented final controls are a confirmation for the consistently high quality. Every product batch has an individual certificate, so there is no need to consider checking the quality of the test kit yourself. In addition, the quality certificates confirm consistent batch-to-batch quality.

For more information

- Spectroquant® test kits see: www.sigmaaldrich.com/test-kits
- Spectroquant® Spectrophotometer see: www.sigmaaldrich.com/spectroquant
- Spectroquant® Prove Connect see: www.sigmaaldrich.com/proveconnect
- MQuant® StripScan see http://www.sigmaaldrich.com/mquant-stripscan

References

1 AbwW, *Verordnung über Anforderungen an das Einleiten von Abwasser in Gewässer*, Anhang 56, in der Fassung der Bekanntmachung vom 21.03.1997, geändert 2017, in BGBI. I 2004, 1124-1125.
2 H. Kim et al, *Concise International Chemical Assessment Document 69, COBALT AND INORGANIC COBALT COMPOUNDS*, Worlds Health Organization, 2006.
3 ISO 11885:2007, *Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*, 2007.
4 DIN 38406-24*, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Kationen (Gruppe E), Bestimmung von Cobalt mittels Atomabsorptionsspektrometrie (AAS)*, 1993.
5 US EPA, Method 200.7, Revision 4.4: *Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry*, 1994.
6 US EPA, Method 200.8, *Revision 5.4: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry*, 1994.

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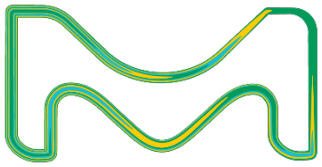

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