Challenge

Reliable measurement of low and high total organic carbon (TOC) concentrations in plating baths of high matrix load like copper, chromium, nickel, palladium or complex metal cyanides.

Solution

Automated TOC quality control of plating baths levels by robust UV persulfate oxidation.

TOC Determination in Electroplating Bath Solutions by UV Digestion

Introduction

Electroplating baths are widely used to deposit a metal coating on a conductive surface by immersion of the objects into a bath solution and application of an electric current. The purpose of this can vary in a wide range that includes decorative silver, gold, or palladium finish on jewelry or the enhancement of physical properties such as corrosion prevention, conductivity, hardness, or durability changes to materials. Manufacturers of plating baths need to establish optimum specifications for their plating solutions and must take action to maintain their formulations and to prevent problems related to improper levels of bath constituents and contaminants. Among other parameters, gradual and continuous changes in cyanide or surfactant content of plating baths may lead to a significant decrease in efficiency. All these problems can be addressed and avoided by monitoring the sum parameter TOC in quality control of plating bath production.

There are two very common principles that can be applied for TOC determination in liquid aqueous matrices: catalytic high temperature combustion and wet chemical digestion promoted by UV light and additional chemical oxidants.

Wet chemical UV digestion is the principle of choice for very aggressive matrices like high salt and/or sulfuric acid concentrations. While the metal salts and mineral acid concentrations may quickly damage the combustion tube and catalyst in catalytic combustion TOC methods, the big advantage of UV digestion is a minimum of maintenance and wear of the TOC system.

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The oxidation power of the multi N/C® UV HS that was used for these measurements is very high due to its high-power, long-life UV reactor. Hence, a complete oxidation of the organic compounds inside the sample is ensured. By application of a TOC differential method, not only the total organic carbon but also the total inorganic carbon (TIC) can be analyzed. It has to be mentioned that inorganic carbon such as cyanides are by definition analyzed as TOC, since the TIC is defined to be the carbon bound in carbonates and hydrogen carbonates which release CO_2 under acid treatment.

Materials and Methods

A TOC analyzer multi N/C® UV HS based on the UV/wet chemical digestion principle was used for the analysis of different electroplating bath samples. Sample introduction was done using the automatic sampling system AS vario.

Samples and Reagents

- Different plating bath samples as well as additives and check samples were analyzed.
- Phosphoric acid 10% (for optional TIC measurement)
- Sulfuric acid 2 M for automatic acidification in NPOC mode and preparation of oxidation reagent
- Sodium peroxodisulphate solution 80 g/L as oxidation reagent

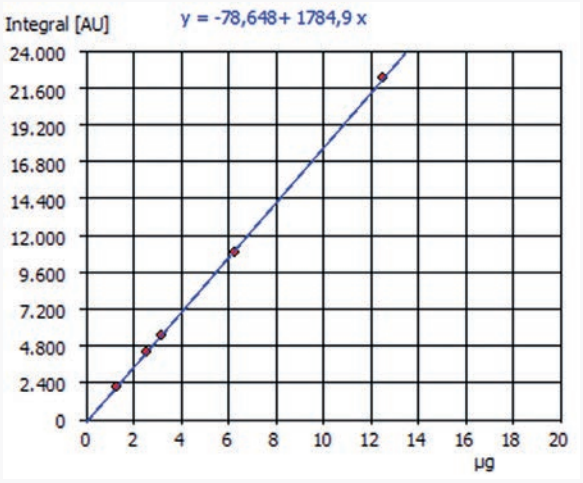
Sample Preparation

Samples were diluted manually before measurement, due to the high viscosity of the original sample. The dilution ratios are shown in table 1. No further preparation steps were applied. Sample acidification can be omitted for NPOC testing in concentrated acids

Calibration

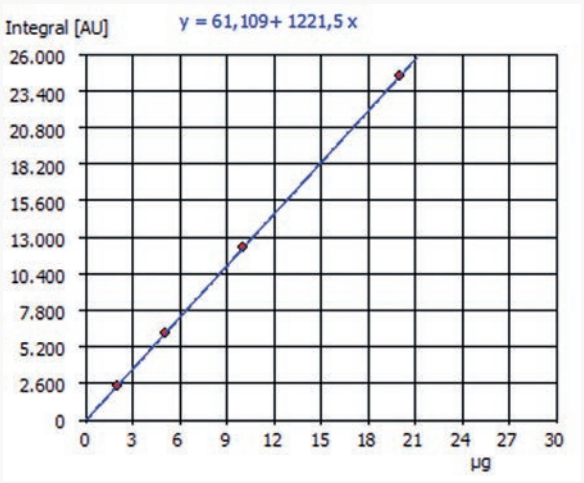
Standards of different concentration levels from 0.5 – 100 mg/L were prepared for TC/NPOC calibration from a 1000 mg/L TOC stock solution of potassium hydrogen phthalate in water and acidified with sulfuric acid. For TIC calibration, mixed standards made from sodium carbonate and sodium hydrogen carbonate (50% each) were prepared from 0.5 – 50 mg/L. A calibration run was started, and linear calibration curves were obtained.

Table 1: NPOC calibration



Residual SD:	78,219AU	Linearity:	OK
Method SD:	17,53µg/l	Variance homogeneity:	OK
Method VC:	0,85506%	Detection limit:	41,70µg/l
Qual. of rep.:	0,99993	Identification limit:	83,39µg/l
Correl. coeff.:	0,99996	Quantification limit:	166,0µg/l

Linear regression and method characteristics for TC/NPOC calibration



Residual SD:	78,68AU	Linearity:	OK
Method SD:	32,21µg/l	Variance homogeneity:	OK
Method VC:	0,69638%	Detection limit:	92,06µg/l
Qual. of rep.:	0,99996	Identification limit:	184,1µg/l
Correl. coeff.:	0,99998	Quantification limit:	395,5µg/l

Linear regression and method characteristics for TIC calibration

Within the method up to 3 calibration ranges can be linked to each parameter in order to cover an over-all working range of up to 3 magnitudes. Detection limits and limits of quantification are depending on the selected working range and can be derived from the method characteristics given above.

Instrumentation

The measurements were performed in the NPOC mode with method settings shown in the below table.

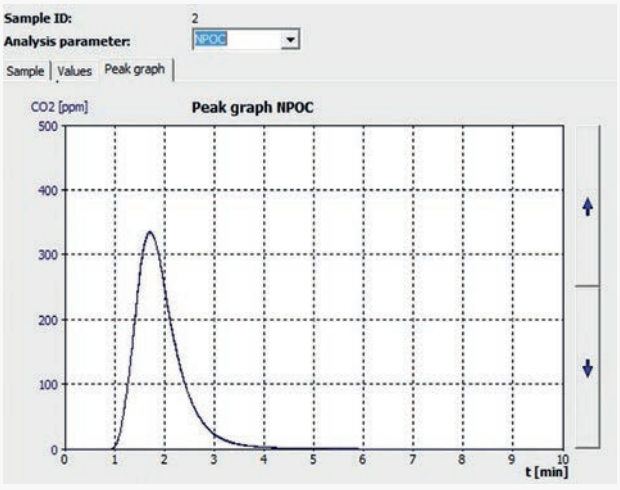
Parameter	Method Settings for NPOC Mode	Method Settings for TOC Mode
Method / Parameters	NPOC + oxidation reagent	TC, TIC, TOC
Digestion	UV / wet chemical oxidation	UV / wet chemical oxidation
Number of replicates	min. 2 – max. 3 injections	min. 2 – max. 3 injections
Rinsing cycles	3 times with sample	3 times with sample
Sample purge time.	180 sec	-
Injection volume	2500 µl	2000

Results and Discussion

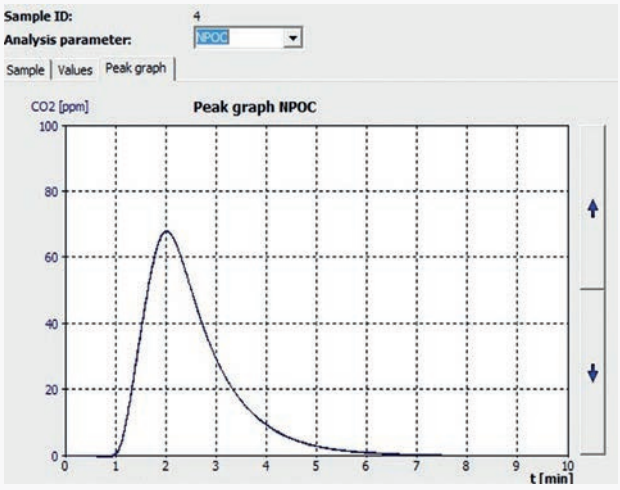
The following table shows the mean values of all conducted measurements calculated from at least duplicate injections, as well as the relative standard deviation.

Table 1: Results TOC

Sample ID	Sample Dilution	Mean Value TC [mg/L] ± RSD [%]	Mean Value TIC [mg/L] ± RSD [%]	Mean Value TOC/NPOC [mg/L] ± RSD [%]
Copper sulfate solution 2	1 in 10	-	-	80.0 ± 0.5 %
Copper sulfate solution 3	-	-	-	0.54 ± 1.3 %
Copper sulfate solution 4	-	-	-	2.9 ± 0.3%
Control Standard 5 mg/L TOC	-	-	-	5.1 ± 0.9%
Na-propensulfonat (10 mg/L)	-	10.58 ± 0.3%	0.19 ± 2.4%	10.38
K[Au(CN)2]	1 in 100	979 ± 0.2%	20.4 ± 4.0%	959
Palladium new - 1	1 in 100	759.7 ± 0.8%	61.9 ± 4.4%	697.8
Palladium old - 2	1 in 100	872.2 ± 0.1%	107.2 ± 1.8%	765.0
Palladium new - 2	1 in 100	786.8 ± 0.1%	76.0 ±2.7%	710.8
Surfactant	1 in 100	1150 ± 0.4%	20.3 ± 2.6%	1130
KHP-Check Standard 1 g/L	1 in 100	1070 ± 0.5%	15.0 ± 2.4%	1055



NPOC measurement Copper sulfate solution 2



NPOC measurement Copper sulfate solution 4

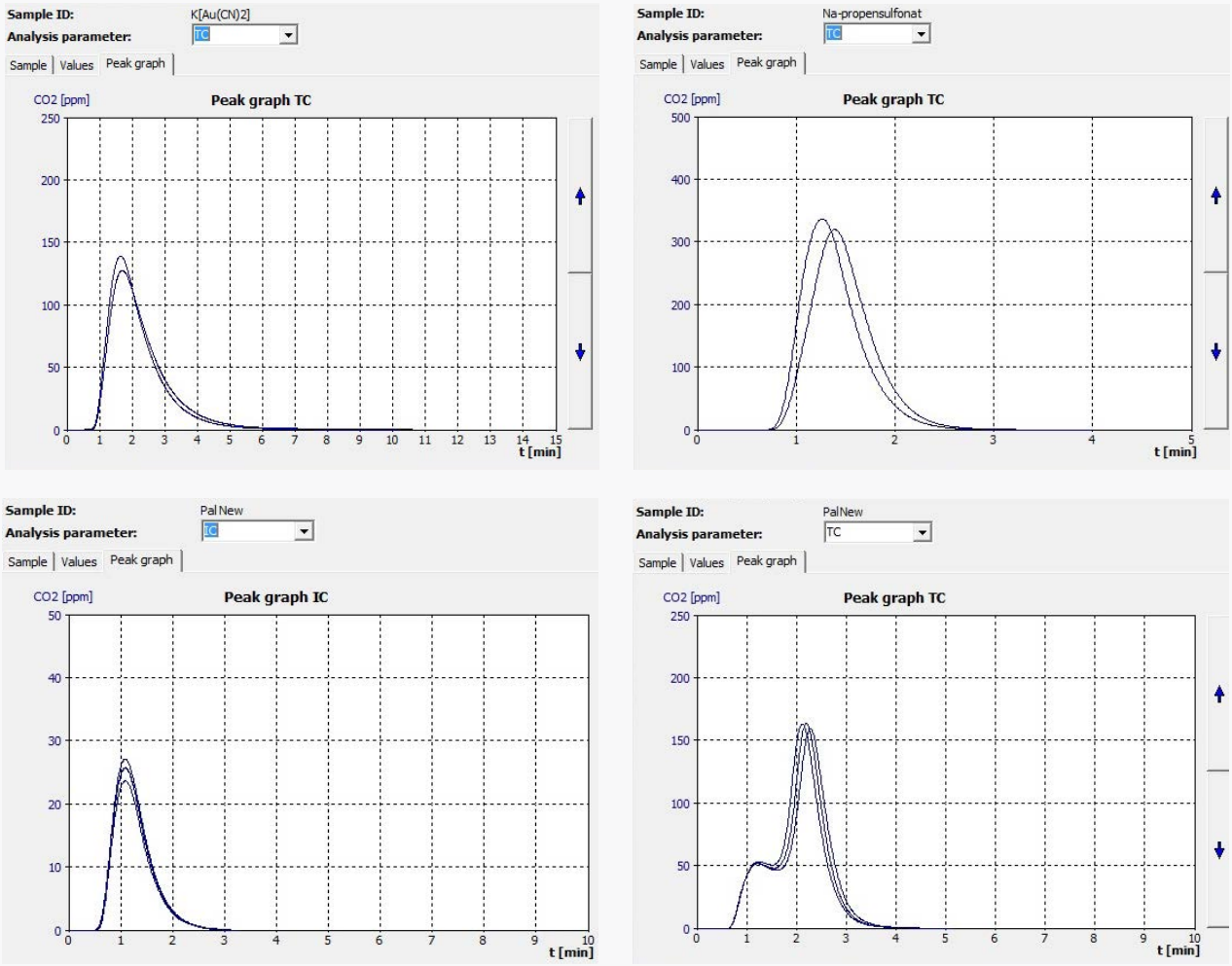


Figure 2: examples of measurement signals for different samples as indicated

Conclusion

With its powerful UV-assisted wet chemical digestion technique, multi N/C® UV HS shows good analytical performance with the samples from electroplating baths. The special reactor design of the multi N/C® UV HS using the energy-rich, short 185 nm UV wavelength in combination with standard 254 nm UV wavelength enhances the complete sample oxidation.

All samples were measured with a very good reproducibility. Together with the low running costs (no combustion tube exchange is needed and high catalyst consumption cannot occur), this makes multi N/C® UV HS the perfect TOC analyzer for TOC analyses of samples with high salt load as well as high acid content (except chlorides and HCl).

By applying the high throughput autosampler AS vario, the parallel purge and analyses feature of multi N/C® analyzers assures short sequence runtimes for the NPOC method and also supports the TOC differential method.

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