Optimum Digestion Technology Enables Affordable TOC and TN_b Detection in Seawater Samples

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The detection of minute TOC and TN_b content in salty matrices, such as seawater, poses a special challenge for many TOC analysers with thermocatalytic digestion. Why? Due to the high salt content with simultaneously low analyte concentrations the sample can often not be diluted meaningfully. In addition the reactor of the TOC/TN_b device is continually loaded with sodium chloride and other salts with every sample injection. With increasing load on the catalyst the measuring results display significantly reduced recovery rates and increased measured value variations. The salt accumulating in the system also rapidly leads to the catalyst and other consumables of the combustion tube becoming useless and having to be replaced after a short period of time.

That there are alternatives is demonstrated by the measurements of deep sea water samples using a device of the multi N/C® series shown below.

Experimental

General

The detection of TOC/DOC (Dissolved Organic Carbon) and TN_b/TDN (Total Dissolved Nitrogen) in deep sea water samples is the focus of global ecosystem monitoring. To this end samples from different seawater currents and layers are commonly analysed. The DOC and TDN concentrations are normally significantly below 1mg/L.

The purpose of the analyses performed was to demonstrate with a long measuring series using deep sea water that the analyser can continually measure very small DOC and TN_b concentrations in a heavily salty matrix with stability and precision without requiring intervention in the digestion system/reactor or other system components.

Material

The analyses for detecting the DOC and TN parameters were performed in a reference material from the university of Miami "Florida Strait at 700m" that was available HCl-stabilised in ampules of 10mL each. The reference material is identified with the following concentration details: cDOC = 492 – 516 µg/L and cTN = 462 µg/L. The salt content is approx. 35 g/kg, with the main component being sodium chloride and sodium sulphate forming the second largest share.

In addition, aqueous calibration standard solutions of potassium hydrogen phthalate and potassium nitrate/ammonium sulphate were used in various concentrations to calibrate the analyser.

Device

All analyses were performed in the TOC/TN_b analyser multi N/C® 3100 (Analytik Jena AG). This is equipped with a chemiluminescence detector for TN_b detection. The measuring device was operated in its default configuration, i.e. without using special reactor consumables or additional halogen traps. For the automatic sample supply the autosampler APG 64 (Analytik Jena AG) was used.

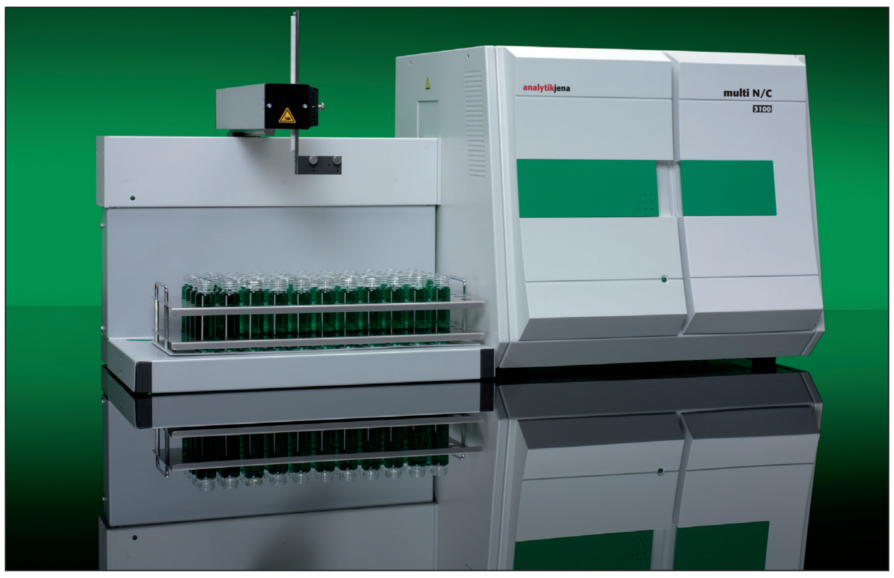

Figure 1: multi N/C® 3100 with APG 64

Method

A method permitting the simultaneous detection of the NPOC and TN_b parameters from a single sample injection was chosen. The sample volume was set to 200µl, the combustion temperature was 750°C. A platinum catalyst supported the combustion.

Procedure

The reference material was first filled into suitable sample cups to allow for an automatic detection of both parameters by the autosampler. Special attention was paid to avoiding contamination by the environment of the only minimally loaded sample material as far as possible. After sealing the cups a complete sampler (64 positions) was filled. After starting the chosen NPOC/TN method the already acidified samples were automatically purged to remove inorganic carbon content (TIC) and dissolved CO_2. Each subsequent sample was purged in parallel with the analysis of the previous sample. This considerably saves time during the analysis process. The samples pretreated automatically in this manner were transferred to combustion via a flow injection system. Multiple injections from a sample cup took place; after every 15 reference samples ultrapure water was analysed to check the blank value of the system.

Results and discussion

The results of the individual reference samples were combined into blocks of five each and are shown in the overview (*Figure 2*). The calculated average concentration value and the standard deviation across all samples were 508µg/L ± 25µg/L (corresponding to a relative standard deviation of approx. 5%) for DOC and 457µg/L ± 17µg/L (corresponding to a relative standard deviation of approx. 4%) for TN_b.

The measuring results achieved match the concentrations of DOC (492–516µg/L) and TN (462µg/L) specified for the reference material excellently. From the stable recovery rates and low measured value variations across a multitude of sample injections can be concluded that no matrix effects on the system can be detected in spite of the high salt introduction. This means that both digestion and detection are stable in behaviour from the first to the last sample.

The ultrapure water analysed after every 15 samples also demonstrated a constant concentration level (DOC < 30µg/L, TN < 20µg/L). This in turn confirms the fact that the introduced salt load did not affect the capability of the system in any way.

After concluding the experimental series the combustion tube was removed and examined for signs of wear. After flushing with ultrapure water and replacement of the catalyst cover the reactor tube could be used for further analyses.

The Specialty – The Digestion Technology

The high stability of the measured values over a long period of time in highly salty samples is in particular due to the digestion technology used in the analyser. A special reactor geometry combined with an optimum temperature guidance prevents the premature and excessive crystallisation of salts on the catalyst and its cover. Dependent on the concentration and chemical nature of the salts introduced these are transported to a colder part of the reactor. No negative effects on the analytical capability are to be expected there. The frequent change intervals of the catalyst – typical for themocatalytic TOC analysers when introducing heavy salt loads – are thus reduced to a minimum.

The quantity of catalyst material used in the combustion tube is very low not least due to the special geometry. Reduced maintenance cycles and low material consumption help to lower the running costs for TOC/TN analysis significantly. Other robust system components contribute to the stability of

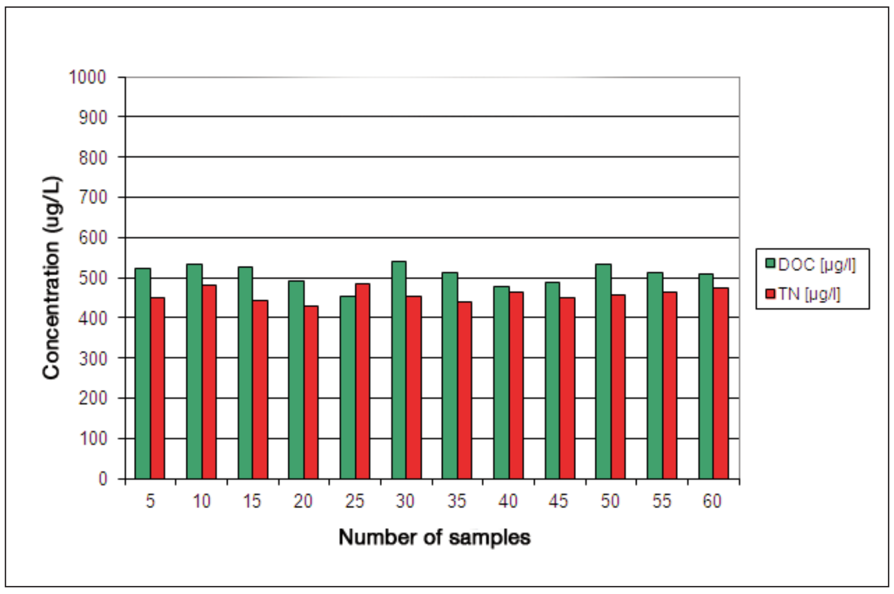

Figure 2: Deep sea water reference material measuring series – excellent stability

the overall system when analysing extreme matrices, such as, the highly sensitive and corrosion-proof Focus Radiation NDIR detector or the VITA® method for flow-independent signal evaluation.

Summary

The results of the analyses demonstrate that using an optimum digestion technology the precise and longterm stable measurement of samples with high salt content is possible. Necessary maintenance intervals can be extended extremely by using a convincing digestion technology.

The expectations of TOC users who often have to measure salty samples include the following requirements for a TOC analyser:

- Numerous sample injections without necessary maintenance intervention in the system
- Self-diagnosis of the TOC analysis system – When is an intervention required?
- Low material consumption when replacing the consumables in the combustion tube
- Easy change of the catalyst/reactor consumables and rapid run-in behaviour for quick measuring readiness
- Low operating costs (due to minimum maintenance effort and minimal use of materials)

With the analysers of the multi N/C® series every user has devices available meeting these requirements.

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New Conductivity Sensor with In-line Calibration Meets Global Pharmacopeia Requirements

Mettler Toledo Process Analytics has launched a new Thornton UniCond® conductivity sensor with in-line calibration capability. It provides a unique solution for fast and accurate in-place electronics calibration - vital to meeting global pharmacopeias - without removing the sensor from the process.

Another major advantage of the UniCond sensor is an ultra-wide conductivity measurement range, from ultrapure water to seawater with one sensor. Stainless steel sanitary sensors have measurement range from 0.02 to 2,000 µS/cm total range with ±1% system accuracy to meet pharmaceutical water requirements.

The UniCond sensor can be used with the Mettler Toledo Thornton M300ISM and M800 multi-parameter transmitters. This enables the use of two or four digital sensor inputs for continuous measurement of ozone, dissolved oxygen, conductivity, pH and total organic carbon.

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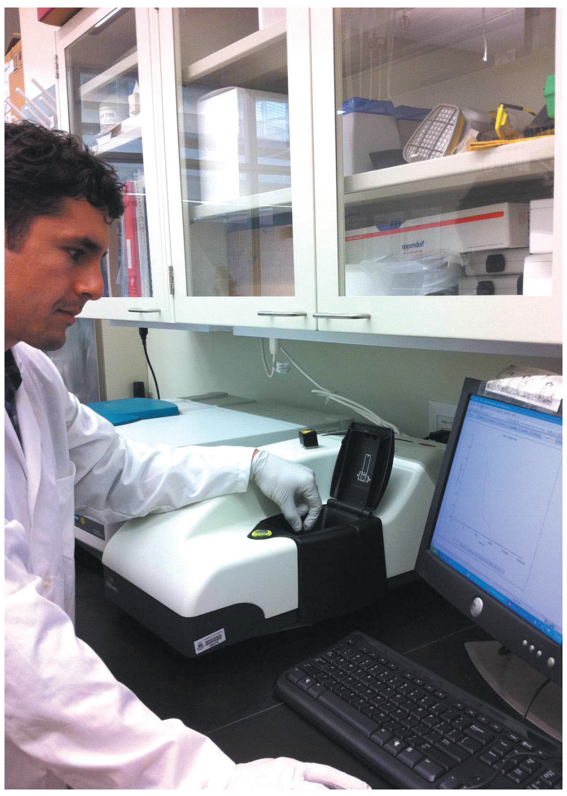
System Delivers Essential Data in Environmental Nanosafety Work



Researchers at the University of Alberta, Canada, working as part of a major Canadian initiative to investigate the aquatic and environmental aspects of nanoparticles, are using the Zetasizer Nano from **Malvern Instruments** to characterise nanoparticle behaviour in biological and aqueous matrices. Size is known to affect nanoparticle toxicity and toxicology and the technique of dynamic light scattering (DLS) provides the average size behaviour in solution. As implemented in the Zetasizer Nano, it delivers information for physical characterisation in terms of charge and solubility.

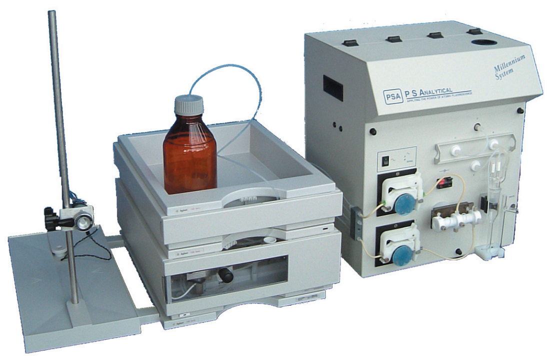
Professor Greg Goss is Director of the Office of Environmental Nano Safety (OENS) in the Department of Biological Sciences at the University of Alberta. "Dynamic light scattering is now recognised as a basic characterisation technique in this area of work and the regulators are familiar with the measurement, its results and limitations. In the past we've used TEM but this works better in conjunction with DLS since we can now study size in solution in a way that is simple to use and with only minimal need for sample preparation," he said. "DLS is the only technique on campus that can provide size information in solution, without drying the samples."

Professor Goss and his team have previously used earlier models of DLS instruments but find that, compared with other systems, the Zetasizer Nano delivers information that is not only much easier to understand and is more consistent, but enables significantly more data interpretation: "We can now study interactions of proteins in ways that previously were not feasible," he confirmed.

The Zetasizer Nano is used by this research group to study the interactions of particles such as silver, titanium, silica and polymer coated quantum dots. Elsewhere in the department it also plays a role in the analysis of other systems, micelles and polymers for example.

MORE INFO. 550

Mercury Determination and Speciation



PS Analytical specialises in the supply of instrumentation for ultra-low level determination and the speciation of environmentally important elements such as mercury, arsenic, selenium, antimony, tellurium and bismuth.

Matrices and applications include water, soils, sludges, effluents and gases. Systems are tailored for customer requirements with worldwide applications support, technical assistance and full-service back up. Systems are available meeting requirements for EPA 1631, 245.1, 245.2 and 245.7, ISO 6978-2, 17852, 16772 and ASTM 6784-02.

Applications for petrochemical analysis for mercury levels remain of significant interest, since mercury, even at low ppt levels creates significant risks to the processing of petrochemical products.

In all fractions of the petrochemical product range, including natural gas, liquefied natural gas and liquid condensates, mercury levels need to be monitored and the mercury removed where possible.

Working closely with industry and regulators, P S Analytical has installed fully automated systems that meet international safety standards and provide continuous measurements of the mercury levels in sample streams.

Tailoring systems and chemistries to customer requirements and site practicalities has put PSA firmly at the forefront of these requirements.

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