

Reprinted from:

AT – PROCESSSM

...the Journal of Process Analytical Chemistry

Advanced Technologies (AT) for Process Analysis

Process AnalyticsSM

JPACSM

SCIENTIFIC REPRINTS

Process Environmental Analysis

Real-Time AnalyticsSM

InfoScience Services, Inc.
3000 Dundee Rd. Suite 313
Northbrook, IL 60062 USA
Tel: 708-291-9161 Fax: 708-291-0097
Internet: infoscience@ais.net

A NEW ANALYZER FOR MEASURING TOC AND TN CONTENT IN SEWAGES

Walter Fabinski, Axel Grunewald, Bernard Hielscher,
Gerhard Wiegleb, and Christian Wolff
Hartmann & Braun, Frankfurt, Germany
and

Wesley Norman, Applied Automation, Bartlesville, OK

ABSTRACT

Due to the complicated matrix of local and industrial sewages, the contents TOC, TN, COD, and BOD have been introduced as summation parameters for characterization and judgment. These measuring methods, taken as basis for these instruments, have been detailed in appropriate guidelines. However, these methods elaborated by the "analytics laboratorium" provide some problems for the continuous on-line application in the environmental and process measurement engineering. For the COD value, the corresponding DIN Instruction NO. 38409 (German Standard) prescribes a two-hour reaction of the sample with extremely toxic reagents. This implies that continuous measuring may be left out of consideration. The discharge of toxic reagents is another problem. In the case of the BOD determination (BOD₅ = five day test), the lag time is a problem.

Upon these considerations, it seems that the "TOC measuring method" has met with greater approval on the part of the users, especially since considerable progress has been made in instrument engineering during the last ten years. But even in this field, some problems had to be solved first. Particularly, the need of maintenance and the frequency of failure of these instruments have, until present, hindered a universal application for a broader circle of users. For instance, various useful monitoring and control functions have been integrated in the newly developed TOCAS, introduced to permit a reliable and maintenance-friendly operation of the instrument. This information is concentrated within the instrument and transmitted as status signals to the user. The first practical experiences with this instrument technique in the industrial application (chemical processing engineering) and in sewage plants confirmed this concept.

BACKGROUND

Pollution control and, increasingly, process optimization are the prime factors for the utilization of on-line analyzers for water monitoring. The recording of certain parameters such as pH, dissolved oxygen, and conductivity in sewage treatment plants is widespread in our present-day practice. These parameters are measured with simple sensors, such as electrodes, frequently inserted directly in the measured medium. Conversely, the widescale on-line measurement of nutrient concentrations and depleting substances is still in the initial stages. This can be attributed primarily to the complexity of the measuring systems. However, nutrient and depleting substances are gaining more attention due to environmental considerations. The depleting substances include organic carbon

compounds, which deplete the oxygen in the water in the course of the self-cleansing process. If the load on the environment is too high, oxygen deficiency results, thus destroying the biological equilibrium.

The measured variables, chemical (COD) and biological oxygen demand (BOD), are frequently used to quantify the oxygen-depleting effect caused by pollutants. The COD determination is a laboratory method, lasting at least twenty minutes, and necessitating the use of environmentally relevant chemicals, such as mercury and chromate. The biological oxygen demand is generally measured as BOD₅, i.e., after an interval of five days. The BOD and the COD show the oxygen depletion under conditions stipulated by the determination method. Even where a high degree of automation is used, these are discontinuous methods and they supply the measurement result with a time lag.

On the other hand, measurement of the Total Organic Carbon (TOC) concentration is continuous and can be performed with very little time delay. The measure of TOC adequately defines an aggregate measurement for organic depleting substances. It entails considerably fewer risks, from the industrial protection viewpoint, and can, to a large extent, be effected continuously without environmentally relevant chemicals. As an aggregate parameter, the TOC concentration bears an empirical ratio to the COD value (the COD value corresponds to 3-4xTOC, depending on the composition of the effluent). It is now, therefore, under consideration to replace the COD value by a TOC limit value in the relevant regulations [1].

Nutrients include nitrogen compounds whose fertilizing effect results in excessive plant growth (eutrophication). The aggregate of the compounds nitrate, nitrite, ammonia, and organically bonded nitrogen is termed Total Nitrogen (TN).

Presented at the 8th International Forum Process Analytical Chemistry - IFPACSM, Houston (Montgomery), TX, January 24-26, 1994.

© InfoScience Services, Inc. All rights reserved.

The TOC and TN concentrations are vital monitoring variables for the operators of sewage treatment plants. Due to the simultaneous and continuous measurement, they serve as environmentally relevant variables. This advantage also occurs in certain biological processes. Process engineering variables can be obtained by combining the TOC and TN concentrations, to be used, e.g., for the optimization of the plant management of sewage treatment processes. For example, a nitrogen treatment plant can be set via the ratio of a TN and TOC concentration. The oxygen demand in the activation tank can be inferred from the sum of TOC + TN. Accordingly, the processes optimized with these variables can minimize their energy costs and, hence, the levies imposed. A consideration to be borne in mind here when implementing an economical measurement technology is the ability to measure TOC and TN simultaneously in a single instrument.

The advantages of the on-line measurement, however, only come into fruition when the measurement is performed with adequate reliability. To this effect, sample conditioning must also be incorporated in the measurement technology.

This discussion presents a combination of long-proven infrared analysis, by an NDIR method, with novel sample handling to yield a practical analyzer to give both TOC and TN. The sample handling also provides diagnostic tools to monitor instrument performance internally. The analysis is available commercially from Hartmann & Braun as the TOCAS analyzer product.

APPARATUS

The instrument employs a thermal principle according to DIN 38409 Part 3 for TOC and DIN 38409 Part 27 for TN. The heart of the TOCAS analyzer is a high temperature furnace combined with H&B infrared gas analyzer technology married with sample handling and control features. Figure 1 illustrates a functional diagram of

the analyzer system. The filtered liquid is conveyed via an overflow vessel to the mixer/stripper by the peristaltic pump. Acid and stripping air are added to the sample water here. A pH electrode is used as a sensor for regulating the pH value. The inorganic CO₂ is taken up by the stripping air; volatile carbonaceous components are also stripped out at this time.

The liquid/air mixture is then separated in a phase separator. The gaseous mixture passes via a cooler to the reference sample cell of the infrared gas analyzer system and, just like the sample water, is conveyed to the thermal reactor. The organic compounds are oxidized to CO₂. The bonded nitrogen is converted into NO. The gaseous mixture passes through a second cooler channel into the measurement cell of the analyzer. The CO₂ measuring channel records the total CO₂, formed from inorganic Total Inorganic Carbon (TIC) and from organic C. In this configuration (flowing reference gas), the gas analyzer itself calculates the difference between measurement results obtained from the measuring and reference channels. Since the gas flow remains in the closed system, the TIC value is formed in both channels and is thus compensated. The measured variable that remains is CO₂ formed from organic C. It is composed of the Dissolved Organic Carbon (DOC), Volatile Organic Carbon (VOC) and Particulate Organic Carbon (POC). This corresponds to the TOC concentration.

In the presence of small measuring ranges and/or large inorganic CO₂ concentrations, the design of the infrared analyzer in the configuration "flowing reference gas" produces an unstable display reading due to time-displaced CO₂ concentrations in the sample and reference sample cell (dynamics). Hence, a CO₂ absorbent is interposed before the CO₂ reference sample cell to fully or partially intercept the inorganic CO₂. Consumption of the absorbent results in an unstable display reading for small measuring ranges; it does not, however, falsify the zero display.

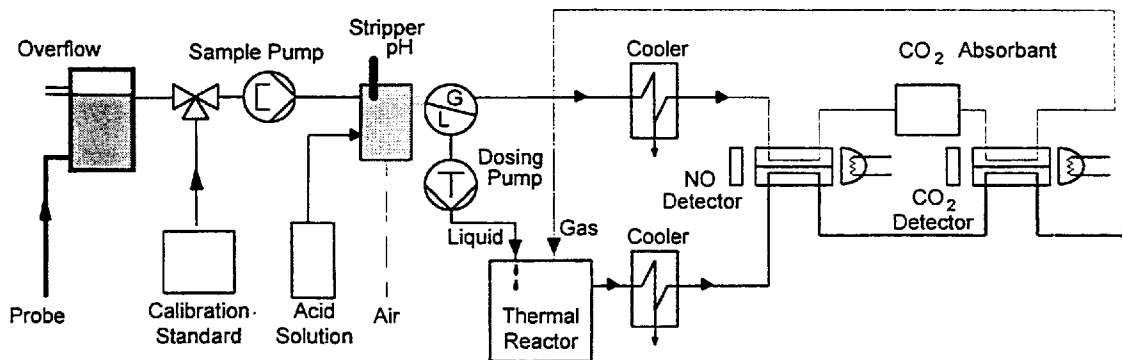


Fig. 1. Functional diagram of the TOC/TN measuring facility.

The TN value is calculated--at the same time as the TOC value--from the NO concentration. Since the NO measurement in the infrared analyzer exhibits a slight cross-sensitivity to water vapor, the cooler is used to bring the sample and reference gas flow to the same dew point.

For the TN measurement, both the inorganic (nitrate, nitrite, ammonia) and the organic nitrogen components are completely thermally converted. Serial measurements have demonstrated that for ammonia, this is the case up to approximately 25 mg/l. At higher ammonia concentrations a noticeable decomposition of NH_3 occurs. Part of the formed NO reacts with the residual NH_3 forming N_2 and water (DeNOx effect). Frequently a certain bandwidth of the ammonia and nitrate concentrations prevails so that, by appropriate selection of an ammonia or nitrate calibration standard, adequate precision can be obtained, even for concentrations of 50 mg/l. Figure 2 illustrates an example. Dilution is necessary if the water contains > 50mg/l of ammonia.

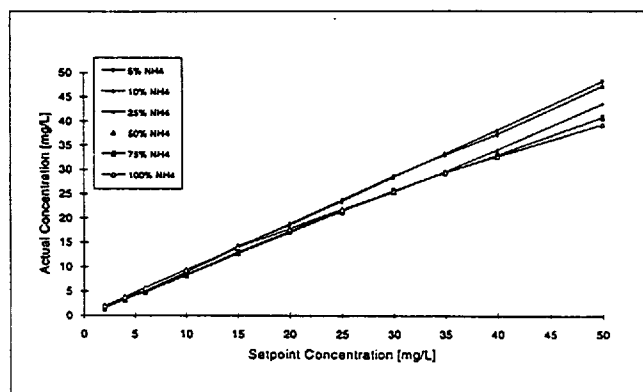


Figure 2. Conversion rates of different ammonia/nitrate mixtures. Used with permission [9].

The long-term precision is governed primarily by the long-term stability of the air quantity and dosing accuracy of the reactor feed pump. Whereas the air quantity can be maintained stable even for long periods by using the commercially available devices such as pressure regulators and pumps, the dosing stability of the liquid needs meticulous care. This pump is exposed to the conditioned sample water and hence to biological, particulate, and acid attacks. For this reason, a piston pump was selected, where the components coming into contact with the water are ceramic and the pump has no valves. The system performance is relatively stable. The drift is less than 4% of the measurement range per week.

The entire measurement procedure is extremely simple and effective. It reduces the fault detection time to a minimum. In the event of a fault, the system is automatically shut down to prevent damage to the components, thereby reducing repair time. Accordingly, the availability of the measuring system is increased, with this being calculated as a quotient of the "mean time between failures" (MTBF) and the sum calculated from the MTBF plus "mean failure time." The measurement credibility is also enhanced by virtue of the automatic calibration with validity check. The distinction made between event-oriented "Maintenance req." and "Failure" also dispenses with unnecessary routine and

immediate inspections on the part of the user [5, 6]. The availability is > 95% (calculated according to VDI/VDE 2180) [7]. Figure 3 is a photograph of the TOCAS Analyzer.

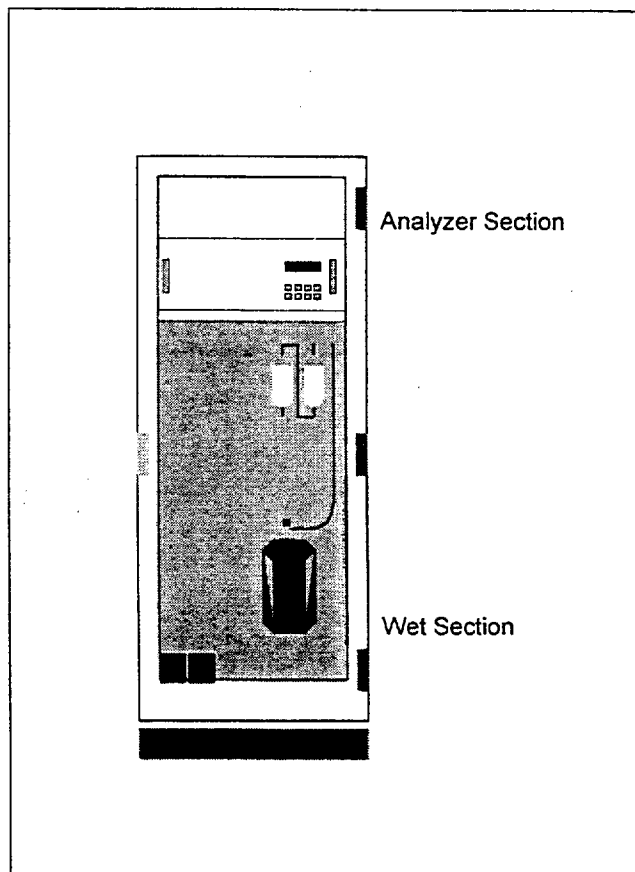


Figure 3. View of the TOC + TN version of Tocas Slide-in unit with recorder and controller; Infrared analyzer with display above. Wet section with cooler, furnace, pumps, filters, valves etc. in the lower section.

EXPERIMENTAL RESULTS

In the course of tests performed at the outlets of different municipal and industrial sewage treatment plants, the values measured with TOCAS were compared with those of a laboratory analysis. A degree of concordance of approximately 95% was achieved between the two methods. The measuring ranges 0-50 mg/l TOC and 0-50 mg/l TN were set in TOCAS. An edge filter with a pore width of 50 μm was used for the sample conditioning. The system was purged once daily with a chlorine bleaching lye to prevent biological growth in the supply lines. The system was calibrated twice daily at the zero and once daily at the span.

The chart in Figure 4 shows an interval from a five month measurement with a zero and a span calibration. A conditioned mixture of potassium hydrogen phthalate and ammonia chloride was used as a standard. To enhance the depiction, purging was carried out with a detergent outside the calibration cycle. Figure 6 depicts the evaluation of the measurement over a period of eleven days. Here, one can easily recognize the daily curves and one weekly curve, particularly noticeable for the TN measurement.

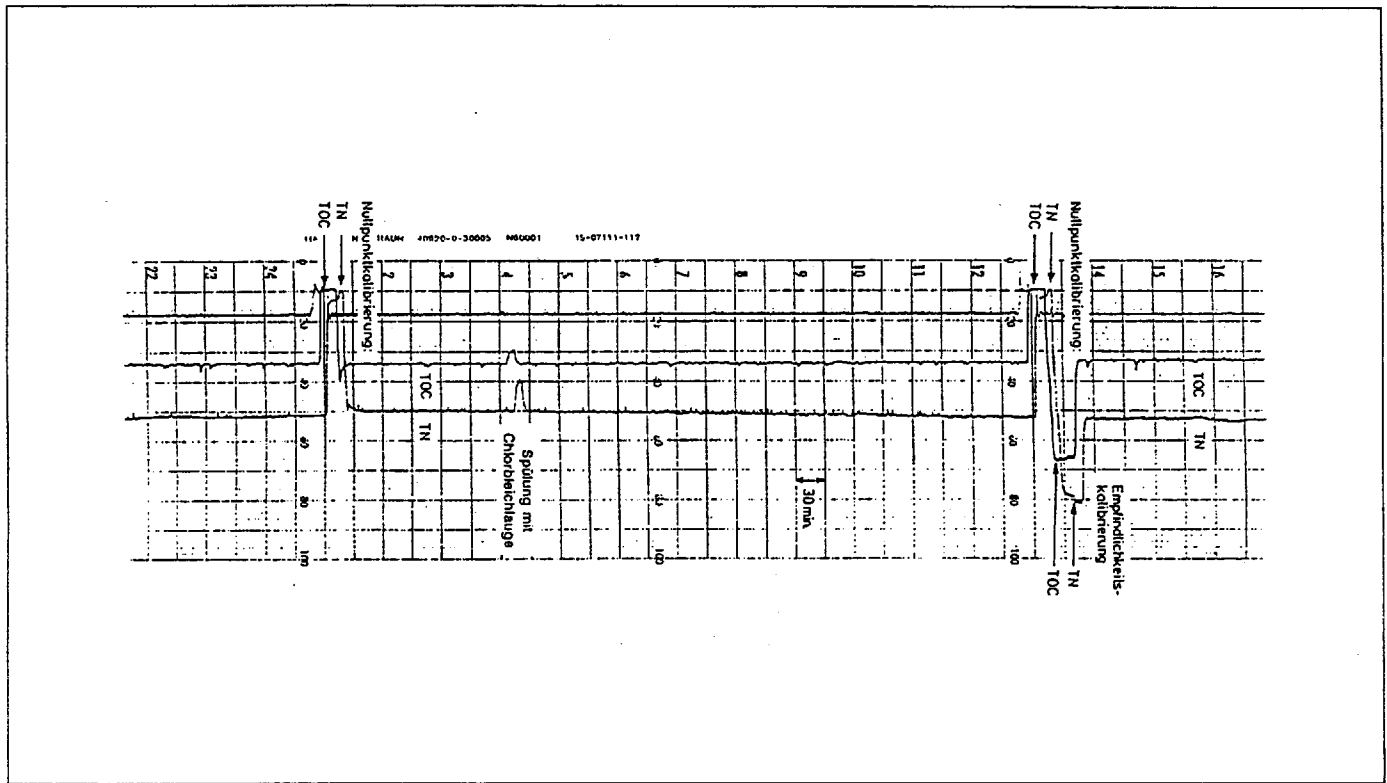


Figure 4. The recorder charts of a measurement performed at the outlet of a municipal sewage treatment plant, featuring a zero and a zero/span calibration. To enhance the illustration, the calibration cycles were prolonged and purging with a chlorine bleaching lye was effected outside the calibration cycle. Used with permission [9].

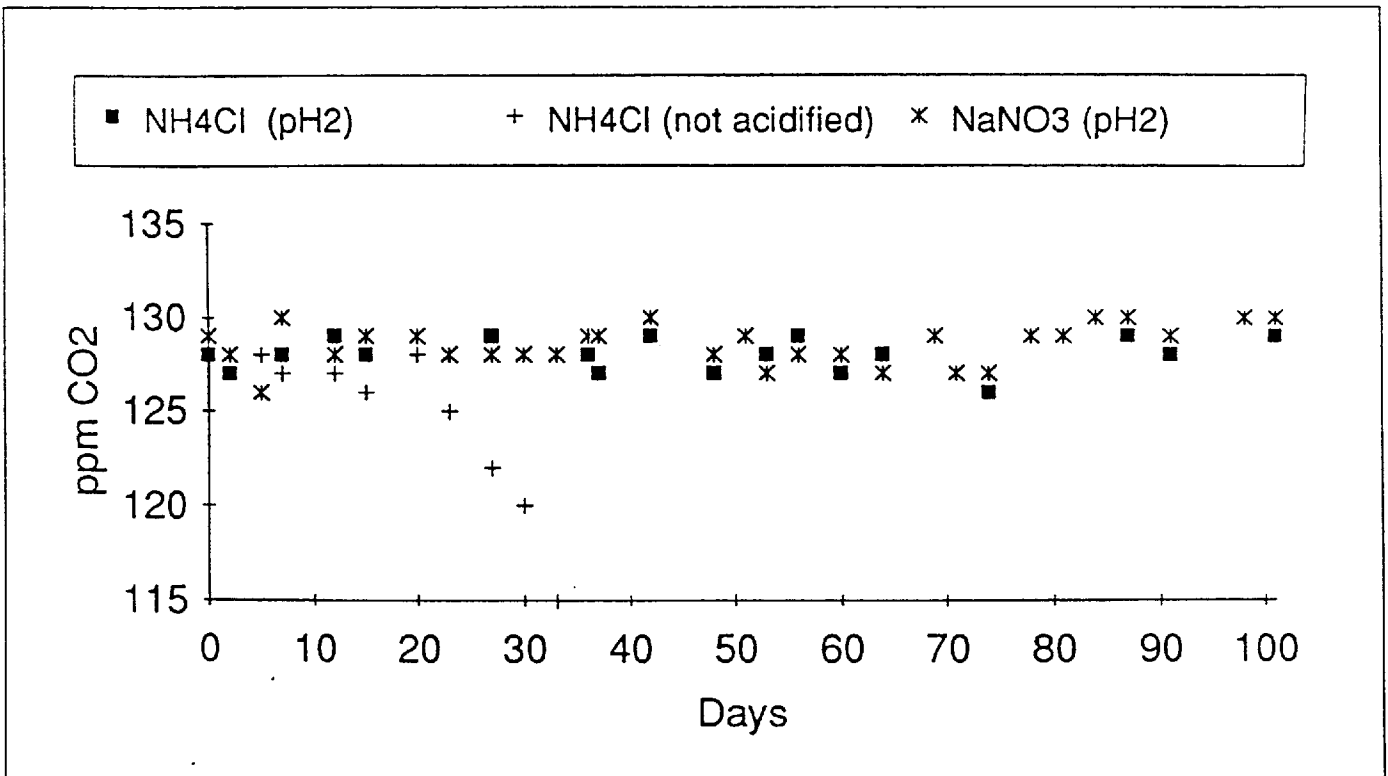


Figure 5. The detected CO₂ concentrations for thermally converted mixtures of potassium hydrogen phthalate (KHP), 25 mg C/l and sodium nitrate or ammonium chloride 25 mg N/l as TOC/TN standards. Two of these were acidified with 1 N HCL to pH=2. Used with permission[9].

CALIBRATION AND DRIFT

Apart from correctly setting zero and sensitivity, the calibration also furnishes data for performing a validity check of the measurements. A precondition to be observed here is that the standard itself must be stable. The chemicals used for these standards are potassium hydrogen phthalate (KHP) for TOC, and sodium nitrate or ammonium chloride for TN. It is common knowledge that solutions of KHP decompose after a short time and are useably stable for one week only if they are stored in a refrigerator. Tests of acidified TOC/TN standards stored at 40 degrees C. showed a long term stability for more than 100 days, whereas an unacidified standard starts to decompose within one week. (See Figure 5).

The following procedure was used in order to effect calibration easily with few mechanical components. For the zero check, both the sampling pump and the dosing pump are switched off so that no water is fed. The air strips out any volatile components still present in the mixer. After a short time, the same concentration is attained in the reference and measuring channels of the gas analyzer and the measuring instrument then operates in the "zero mode." A deviation from "Zero," caused, e.g., by aging of the gas analyzer, sample cell contamination or by a change in the cooler temperature, is now aligned by the calibration step "Zero calibration" of the measuring instrument. Neither "Zero water" nor a special solenoid valve is needed for this step.

In a second step, the sample pump and the dosing pumps, as well as the calibrant solenoid valve, are activated (see Figure 1) for the sensitivity alignment. The calibration solution conveyed by this action produces a deflection that can be used to readjust the sensitivity. By virtue of the closed measuring system, calibration is assured to the same extent for both volatile and dissolved components. Figure 4 illustrates a calibration procedure. A twelve hour calibration interval is set, with zero and zero/span calibration being performed alternatively. During calibration, the measuring instrument ascertains the deviation with respect to the preceding zero and span settings. In the event of

infringement of the alarm values specified for these deviations, implausible instrument states can be detected and reported in this manner [5].

MAINTENANCE AND DIAGNOSTICS

Water, acid, and air are introduced into the measurement process. If there is malfunctioning of one mechanical component, it could result in incorrect measurements, a breakdown of the measuring system or, in the worst case, in damage to the instrument system. Therefore, the complex interaction of the mechanical components involved in the measurement process calls for detailed monitoring and for a shutdown of some mechanical components, for their protection.

The monitoring and logic control concept has been integrated into the gas analyzer, with the microprocessor-controlled gas analyzer featuring the necessary hardware and logic. This means that a uniform display and operation concept is possible for the entire measurement system.

The gas and liquid monitoring facility demonstrates these points. Monitoring is performed in the gas analyzer by means of a pressure sensor. In the tubing system, the gas flow produces a drop in pressure that is compared with specified maximum and minimum setpoints. As the liquid is introduced drop by drop into the furnace, it produces pressure surges in the tubing system on evaporation. These pressure surges are passed via the sample gas lines into the gas analyzer and add to the pressure prevailing in the gas flow. The pressure sensor records these variables. In the processor, the pressure surge sequence is evaluated as a frequency and compared with a setpoint. Depending on the deviation, "Maintenance req." or "Failure" is triggered. Under some failure conditions, gas or liquid pumps are switched off, thus preventing damage to the instrument and an error message is output.

The breakdown of relevant mechanical components is reported and, if there is danger of damage or destruction, endangered mechanical components are shut down.

Some studies have been made to characterize the expected routine maintenance. See Table 1 for details.

Table 1. Approximate maintenance intervals

Type of Maintenance	Frequency of maintenance at the outlet of waste water plants
Thermal Reactor Depending on salt content; once a month for undiluted sample with salt content > 2g/l.	2/annum
Peristaltic Pump Tubing	4/annum
Carbon dioxide absorber For CO ₂ concentrations in air < 1000ppm.	4/annum
Chemicals	12/annum
2.5% HCl	6/annum
calibration standard	

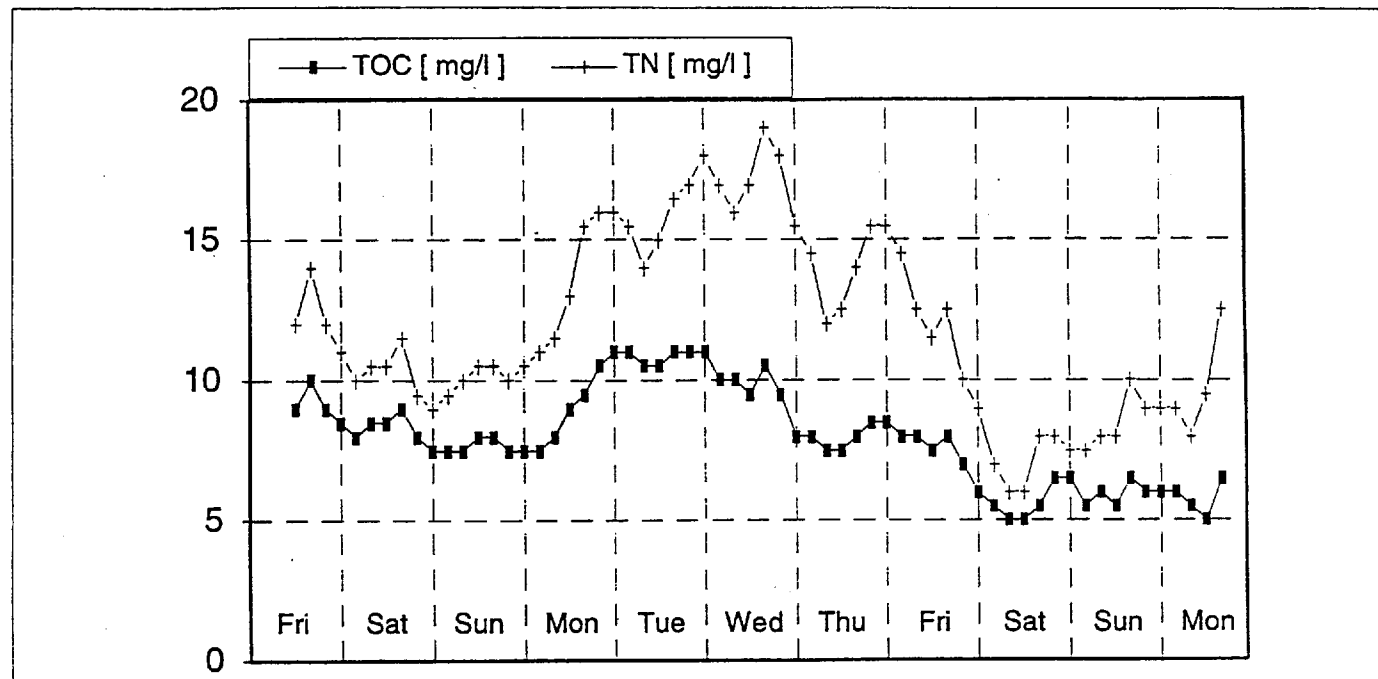


Figure 6. Evaluation for the TOC and TN measurement with Tocas at the outlet of a municipal sewage treatment plant over a period of 11 days. Particularly noticeable are the daily curves and the weekly curve for the TN concentration. The values are obtained with a 50 μm edge filter. Used with permission [9].

SUMMARY

The implementation of the measurement concept with a minimum number of mechanical components results in a simple, well integrated equipment technology that fulfills the requirements of TOC and TN monitoring in sewages. The instrument data can be summarized as follows:

- simultaneous recording of TOC and TN values in a single instrument
- calculation of the TOC value as the sum of volatile (VOC) and dissolved Carbon (DOC) (Simultaneous recording of the TOC depends on the type of interposed filter)
- consumption of the absorbent has no effect on the zero
- automatic calibration; no zero water
- simple and comprehensive monitoring concept by virtue of closed-system design
- low energy costs

The employment of a thermal decomposition process results in a uniform sample conditioning for both measured parameters. The gaseous products are measured in an infrared gas analyzer designed here as a two-component instrument. This instrument also performs the majority of the self-monitoring tasks and outputs them on the display or via an interface as necessary. Hence, simultaneous measurement of TOC and TN can be performed in a single instrument, with less investment than for two separate instruments and relatively few mechanical components, while taking account of the specified demands. These features are a precondition for a high degree of availability and a long service life, as well as for an attractively priced solution. In tandem with a sample conditioning facility especially geared to the measuring task, TOCAS thus constitutes a measuring systems for

environmental and process use.

REFERENCES

1. J. Hahn, MeBinstrumentarien im Bereichwasserrechtlicher Regelungen. UTA No. 1 (1992), No. 2 (1992), and No. 3 (1992).
2. Council Directive of 21.05.1991 Governing the Treatment of Communal Effluents (91/271/EEC). Published in the European Community Gazette No. L135/40 of 30.05.1991.
3. Patent Document DE 41 15 425 C1.4. M. Ascherfeld, W. Fabinski, and R. Vogt, Erweiterte Möglichkeiten und Anwendungen mit dem NDIR-Fotometer Uras 10E. Techn. Messen 57 (1990) No. 1, pp. 11-17.
5. W. Fabinski and E. Muller, Die automatische Überwachung, Steuerung und kalibrierung kkomplexer On-Line-MeBeinrichtungen am Beispiel des neuen TOC/TN-Analysators Tocas. Messen Prüfen Automatisieren (mpa) (1993) No. 3, pp. 10-12.
6. H. Raab and A. Wachter-Buchner, Kontinuierliche TOC-Meßtechnik in der Abwasserüberwachung. atp-Automatisierungstechnische Praxis 34 (1992) No. 3, pp.128-136.
7. VDI/VDE 2180 Blatt 2, Berechnungsmethoden für Zuverlässigkeitskenngrößen von Sicherungseinrichtungen, April 1986.
8. H&B Document, Liquid Analysis. Effluent Sampling, Technical Information 30/22-100 EN.
9. W. Fabinski, A. Grunewald, B. Hielscher, and C. Wolff, Die kontinuierliche On-Line-Messung des organischen Kohlenstoffs und des gebundenen Stickstoffs in ab- und Prozeßwassern mit dem Tocas "gwf-Wasser/Abwasser" 134 (1993), Vol. 10, pp. 613-619.