TOC 8

TOC-ANALYSIS OF DRINKING WATER

Dipl.Chem. G. Bäurle, Shimadzu Deutschland GmbH, Duisburg

The importance of drinking water is undisputed. That fact is underlined, too, by the great number of german laws and regulations considering this topic. Water is classified into different qualities [1]. Besides tap water, there is natural mineral water, medical draft water, spring water and soda water. Every water shows defined characteristics and qualities and is distinguished in particular by the method of its production. For the production of drinking water, for instance, different additives [2] are allowed. Among others, chlorine, chlorine dioxide and ozone are used for disinfecting.

If there is a considerably high content of organic carbon compound in the water to be processed, Trihalogenmethane will develop as a result during this step. The concentration of those are supposed not to exceed 0,025 ppm. A previous determination of the organic carbon compound can facilitate compliance with this limit.

In the following application a variety of most different fountains and drinking water samples from different countries were examined for their TOC content.

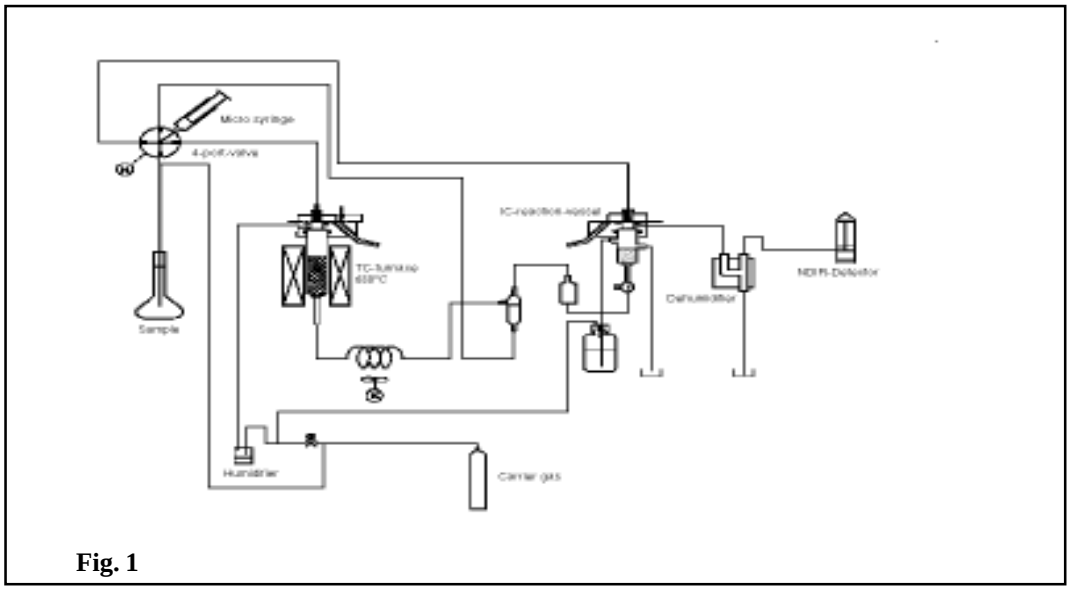


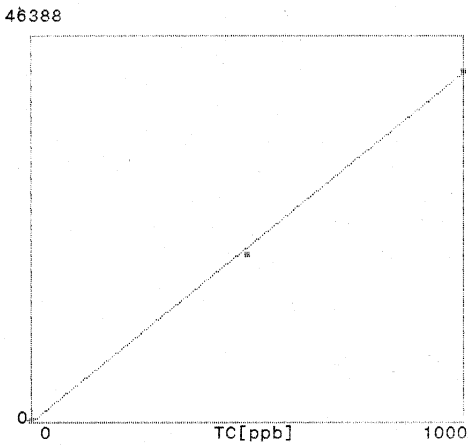
Fig. 1

TOC-5000A

The flow chart of the TOC-5000A of Shimadzu is shown in Fig. 1.

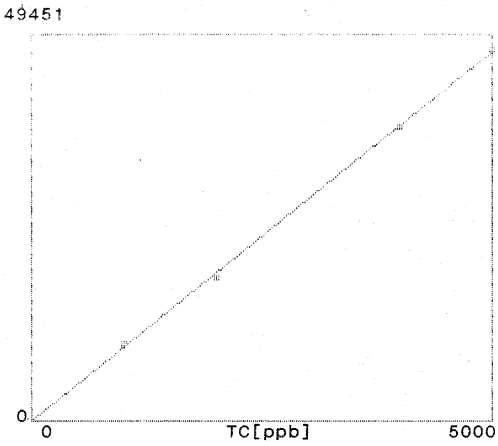
As to be taken from the flow chart the device works with a catalytic oxidation at 680 °C for the TC determination. In order to achieve the large effective measuring range of the equipment of 4 ppb to 4000 ppm, two different catalysts are used. A platinum catalyst is used for ultra pure water. In this case the active component was added to silica glass wool. In the waste water sector, a platinum catalyst, whose carrier material consists of aluminum oxide, is employed. On account of these differences, injection volumes between 4 to 2000 µl might be used, depending on the calibration range of the device in connection with the amplification factor of the detector.

The determination of the inorganic carbon occurs by injection of the sample into phosphoric acid. The resulting carbon dioxide is degassed from phosphoric acid with the aid of carrier gas and quantified with NDIR, according to the TC determination.




```
CAL CURVE F# 3
 TC 3-POINT  (SHIFT TO ORIGIN)
 PROTECTED
 LEAST SQUARES r=1.000

 [CONDITIONS]
   TC CATALYST          : HIGH SENS
   INJ VOL/SYRINGE SIZE: 533/2500µl
   RANGE                : x1
   SPARGE TIME          : 0min
   NO OF WASHES         : 3
   DATE                 : 02(FEB)-09-1996
 [DATA]
   STD CONC    AREA #INJ   SD    CV
    1000ppb   46388  3    203 0.43%
   500.0ppb   24452  3    282 1.15%
     0.0ppb    4387  3    173 3.95%
```

Fig. 2a:
TC Calibration from 0 - 1000 ppb



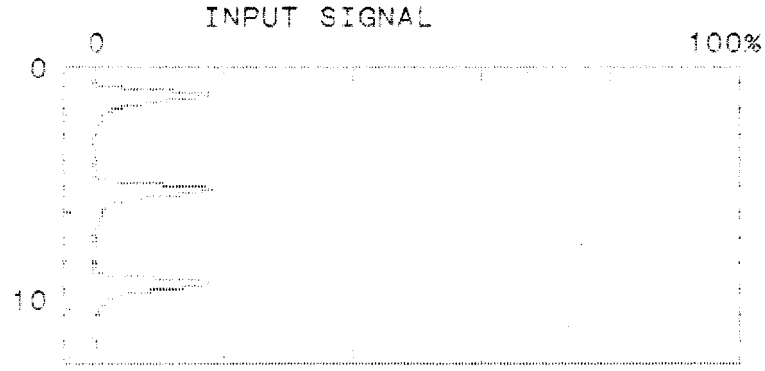

```
CAL CURVE F# 5
 TC 4-POINT  (SHIFT TO ORIGIN)
 LEAST SQUARES r=1.000

 [CONDITIONS]
   TC CATALYST          : HIGH SENS
   INJ VOL/SYRINGE SIZE: 106/2500µl
   RANGE                : x1
   SPARGE TIME          : 0min
   NO OF WASHES         : 3
   DATE                 : 02(FEB)-13-1996
 [DATA]
   STD CONC    AREA #INJ   SD    CV
    5000ppb   49451  3    916 1.85% H
    4000ppb   39524  3    718 1.81%
    2000ppb   20269  3    256 1.26%
    1000ppb   11965  3    201 1.67%
```

Fig. 2b:
TC Calibration from 1000 - 5000 ppb

Calibration

TC calibration was done in the range of 0 to 1000 ppb and 1000 to 5000 ppb, with Potassium-biphthalat at 680 °C [3]. The TC calibrations are shown in figures 1a and 1b.

In order to inspect the inorganic carbon content after degassing a calibration between 0 and 1000 ppb with standards containing a mixture of sodium carbonate and sodium hydrogen carbonate was done.




```
TIME [ min ]

SAMPLE#    1 NPOC  VIAL:  1
 [x 1,  106µl, C#  5, #WASH 3, SP 20min]
    #  AREA ppb      C#  µl RG
    1 11598   1229
    2 11781   1249
    3 11353   1203
  - - - - - - - - - - - - - - - -
   MN 11577   1227
   SD   214  22.77
   CV  1.85 %
   COR CONC DIL    1227 [x 1.0]
   COR CONC INJ    1227 [x 1.0]

        DATE  02(FEB)-15-1996  10:33
```

Fig. 3a:
NPOC - Analysis of Surface water from Greenland

Analysis method

The samples were examined for their organic part by means of NPOC. This method determines the organic content after the removal of inorganic carbon. That means that the samples with hydrochloric acid was acidified to a pH-value of 1 - 2 and subsequently degassed making use of a carrier gas. Because carbonates are not stable anymore with this pH - value and, therefore, form carbon dioxide, the inorganic carbon can be removed by degassing.

Subsequent, those organic carbon contents of the sample which can not be blown off are converted to carbon dioxide by means of catalytic oxidation with 680 °C and quantified with the aid of the NDIR method. Using this method it is especially important that the pH-value is kept, since otherwise the conversion of the carbonates to carbon dioxide does not happen completely and/or too slowly and as a result is not removed completely during the degassing time.

In this case inorganic carbon is determined as organic. Therefore, the TOC-5000A/ 5050A features a measuring routine which combines the NPOC method with a following IC check and subsequently checks if the inorganic carbon is completely removed.

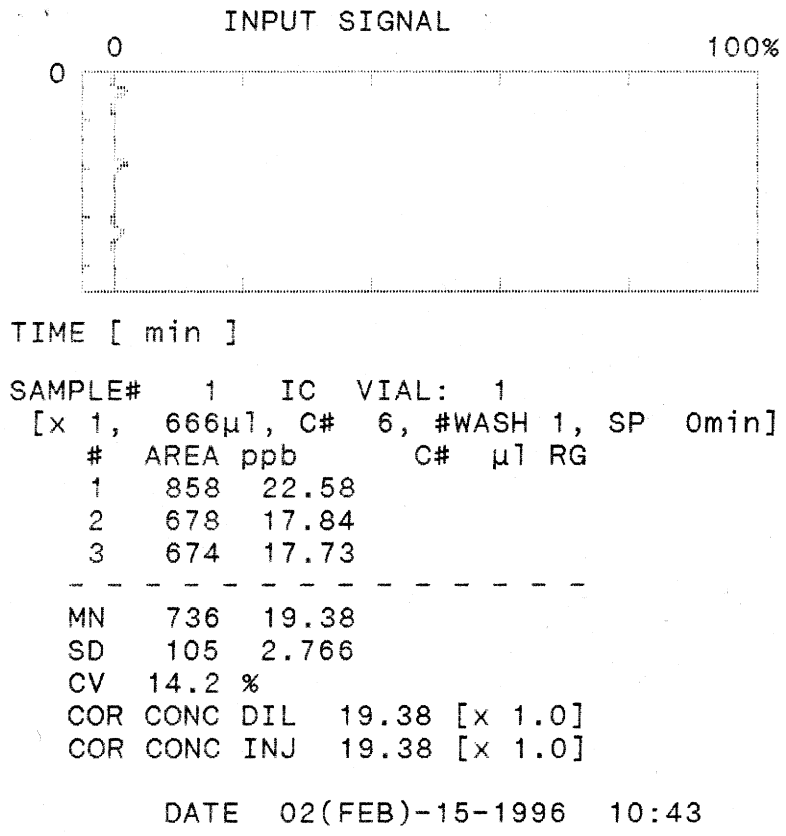


Fig. 3b:
IC - Check subsequent to the NPOC - analysis of the Greenland water

How to do the Analysis

Drinking and well waters from different countries were examined for this application. The origin of the different water samples is shown in table 1. This sort of samples usually have a very great part of inorganic carbon (in relation to the TOC content), so that it is not reasonable to apply the difference analysis. For this reason the organic carbon which can not be blown off was determined in these samples. Illustration 2a and 2b show the analysis of the Greenland water. The analysis conditions are to be seen in the report. In addition to the conditions which were taken from the calibration (measuring range 1 and injection volume of 106 µl belongs to it, too), the degassing time is reported with 20 minutes.

Country of Origin	Type of Water	NPOC-Result [ppb]	IC-Check [ppb]
Greenland	Surface water	1227 ± 23	19 ± 3
Spain	Tap water	2916 ± 70	50 ± 5
Turkey	Tap water	3668 ± 26	30 ± 5
India	Tap water	1515 ± 22	37 ± 3
Hungary	Tap water	1739 ± 37	39 ± 4
Guinea	Tap water	1313 ± 20	12 ± 2
Germany	Tap water	2383 ± 45	13 ± 3
Nigeria	Well water	950 ± 20	12 ± 2
Tschechia	Tap water	1550 ± 21	12 ± 4
Romania	Well water	782 ± 16	19 ± 5
Romania	Tap water	1032 ± 10	12 ± 4

Table 1

Analysis results and discussion

The analysis results are shown in table 1. In addition to the NPOC results, the values for the IC check are stated, too. That check was done directly from the same sample, following the NPOC analysis. The results for the IC check show these values laying in the normal error range of the NPOC results and, therefore, may be neglected. Therefore, the degassing time of 20 minutes can be considered as sufficient.

The difference between fountain water and tap water, concerning the TOC content, is to be recognized clearly. It is also pretty clear that the TOC content in tap water of the different countries of origin vary widely. The total range of the organic carbon contents varies between 1 to 3,7 ppm. These differences illustrate that the further processing of the water can be planned more efficient if the organic carbon content is known beforehand. Another advantage is that the expenditure for the TOC analyses is not very big.

For the analysis of drinking water a sample preparation is not necessary. Also, the acidification of the samples can be automated with the auto sampler.

Literatur

[1] Das neue Wasserrecht für die betriebliche Praxis,
07/4.4.3 Mineral- und Tafelwasserverordnung, WEKA Fachverlag

[2] Das neue Wasserrecht für die betriebliche Praxis,
07/4.2.1 Trinkwasserverordnung § 5 (1), WEKA Fachverlag

[3] DIN 38409 Teil 3; Bestimmung des gesamten organisch gebundenen Kohlenstoffs (TOC)

Instrumentation

Shimadzu equipment:	TOC-5000A
Carrier gas:	ultrapure oxygen or synthetic air
Oxidation:	catalytic Ox. 680 °C with high sensitive Cat.
Method:	NPOC with IC inspection

02./E/09/97/GBB/bmu

Shimadzu Deutschland GmbH
Albert-Hahn-Str. 6 - 10, D-47269 Duisburg
Telefon: (0203) 76 87 - 0
FAX: (0203) 76 66 25