TOC 4

TOC DETERMINATION IN SLUDGE

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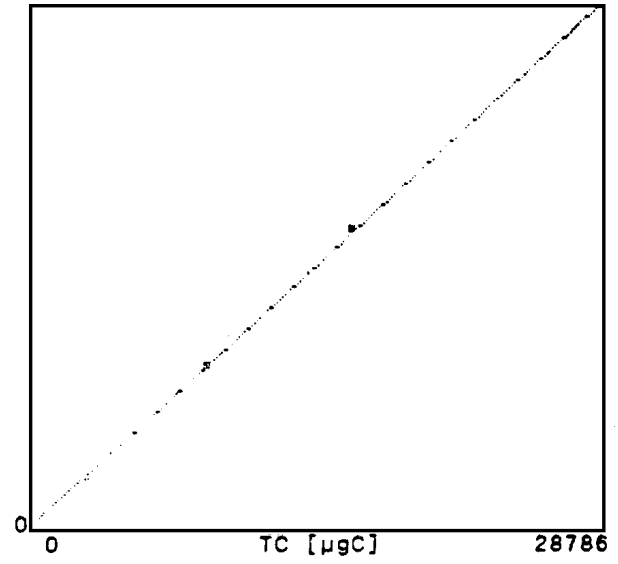
To characterize and limit the amount of organic substances in waste the TOC-parameter (total organic carbon) was incorporated as determination parameter in the new TA Siedlungsabfall (TA: Technical instruction, June 1st 1993). This sum parameter which is a firm component in the water analysis already for years also becomes more and more important in the solid sample analysis. In this case, the waste depending on the content of TOC is assigned to different dump classes.
In order to be classified under dump class 1 (mineral material dump) the waste may at the most include a TOC content of 1 mass percent of dry residue. For rating in dump class 2 (settlement waste dump), a maximum of 3 mass percent of dry residue is permitted.



CAL CURVE F#10
TC 4-POINT
LEAST SQUARES r=1.000

[CONDITIONS]
RANGE : x30
CELL LENGTH : STD
DATE : 08(AUG)-09-1994

[DATA]

STD CONC	AMNT	µgC	AREA	#	
40.0%	71.96mg	28786	23535	3	
40.0%	40.16mg	16066	13697	3	
40.0%	21.76mg	8706	7484	3	
40.0%	6.767mg	2706	2279	3	P

Instrumentation

The determination was done by use of the Shimadzu TOC-5000 with the solid sample module SSM-5000A. On account of the present concentration areas in the solid substance the short measuring cell (0,4 mm of length) was used in the TOC-5000.

Ceramic boats, which are supplied with the device, were used as sample vials.

Measuring conditions

TC oven temperature:	900 °C
IC oven temperature:	200 °C
Carrier gas pressure:	3 bar
Carrier gas flow rate:	0,5 l/min

Fig. 1: Four point calibration with Glucose

TOC analysis

Two procedures are well established in the TOC water analysis for TOC determination: the difference method and the direct method.

In the case of the difference method the total carbon content (TC = total carbon) and the inorganic carbon content (TIC= inorganic carbon) are determined in two independent measurements. The organic carbon to be determined is then calculated from the difference of these two results.

In the case of the second method, the organic carbon content is determined after the removal of the inorganic carbon. The solid sample is first acidified then heated up and dried again in order to remove the inorganic carbon. The remaining content of carbon from the dried sample is then determined by a total carbon analysis and compared with the content of organic carbon. As was shown in previous investigations /2/, the direct method often leads to less valuable results which are e.g. caused by acid reactions.

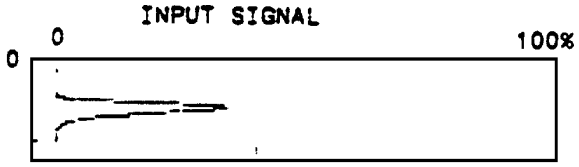
With consideration of the above mentioned reasons, the difference method was applied for this investigation. The TOC determination occurred at an oxidizing temperature of 900 °C, using ultra pure oxygen. A post-connected catalyst which consists of a composition of cobalt oxide and platinum on aluminum oxide guaranteed a complete oxidation of the gaseous components.
The inorganic carbon was transformed to CO_2 at a temperature of 200 °C under use of concentrated phosphoric acid.

In both cases, the resulting CO_2 was determined quantitatively by means of the NDIR method.

Calibration

The calibration of the TC range (range 30) was done with Glucose, since it is available to very high degrees of purity and is oxidized fast and completely. Sodium carbonate was used for the calibration of the inorganic carbon.
Illustration 1 shows the four point calibration in the TC range. The Glucose employed for the calibration has a carbon content of 40% which results in a calibration range of between 2,7 mg to 28,8 mg of carbon (absolutely) at weight-in quantities between 6,7 mg to 72 mg. As to be recognized in the illustration a correlation of 1,000 occurs within this range. The verification of the calibration is represented in illustration 2. In this case, a content of carbon of 40.40% was determined for Glucose. That means a recovery rate of 101 percent.

The calibration of the inorganic carbon was done by use of Sodium carbonate - as shown in figure 3 - in a range between 0 to 0,7 mg carbon (absolute) since the content of inorganic carbon in sludge's is usually very low. This calibration range with a correlation factor of 0,9999 is to be considered linear, too.

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SAMPLE#   1   TC
 [x30, C# 10, DENSITY   1.0mg/µl]
    #  AREA %      AMNT(mg)
    1 11448 40.40 33.90
  - - - - - - - - - - - - - -
   MN 11448 40.40 33.90
   SD       0.000
   CV        0.00%
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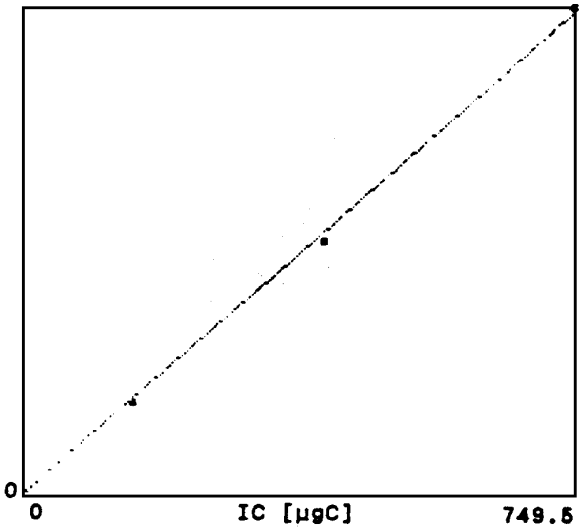
Fig. 2: Calibration check

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CAL CURVE F#11
 IC 4-POINT
 LEAST SQUARES r=0.999

 [CONDITIONS]
   RANGE                : x1
   CELL LENGTH          : STD
   DATE                 : 08(AUG)-10-1994
 [DATA]
   STD CONC    AMNT      µgC  AREA  #
    11.3%    6.633mg 749.5 16562  3
    11.3%    3.633mg 410.5  8671  3
    11.3%    1.367mg 154.4  3265  3
    11.3%      0.0mg   0.0   219  2
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Fig. 3: IC - Four point calibration with Sodium carbonate

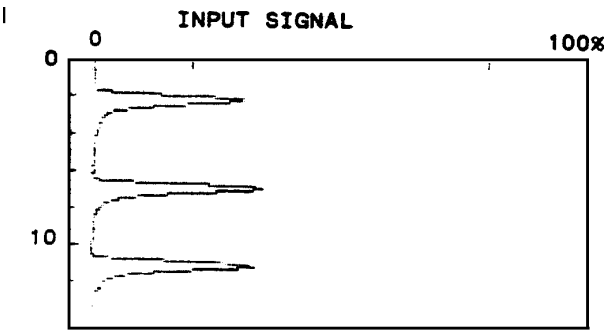
Results

Two different sludge's were tested for their content of TOC for this application. Sludge 1 was examined both, in the original state and after the filter press e. g. after the thermal drying process.

Figure 4 shows the typical peak form of a TC analysis and a fast and complete oxidation can be assumed. The peak is detected within an analysis time of approximately four minutes, whereof the actual oxidation time conducts only two minutes, as to be seen in the illustration. The complete oxidation is proven by it's good repeatability and also by the fact that there is no tailing which is usually the result of an incomplete reaction fading away very slowly.

Such a reaction is to be seen in figure 5 which shows the IC measurement of the same sample. Looking at the peak forms it is easy to recognize that the conversion of the inorganic carbon to CO_2 by use of phosphoric acid did not occur completely. That is especially obvious in measurement 3 where not only one peak was produced but another one was detected after reaching the baseline. That leads to the conclusion that the phosphoric acid could not resolve the coarse particles. The conversion of the inorganic carbon occurred first in the smaller sample particles and then in the bigger ones. But not only the peak form of these measurements show the incomplete conversion very clear. The bad repeatability of the individual measurements shows that the test result should be double checked again.

In the case of the determination of the inorganic carbon, it is very important that a good mixture with phosphoric acid is guaranteed. The acid reaction will be very slow if the sample consists of coarse particles. This causes often minor results because the acid can't convert the inorganic carbon within this particles into CO_2 .

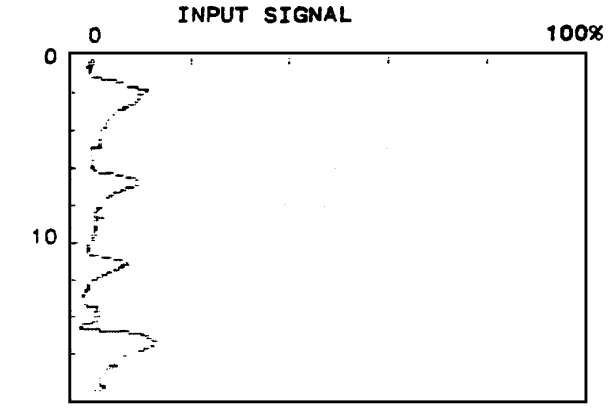


TIME [min]

SAMPLE# 2 TC
[x30, C# 10, DENSITY 1.0mg/µl]

#	AREA	%	AMNT(mg)
1	11061	11.94	110.7
2	11716	12.26	114.4
3	11820	12.20	116.0
MN	11532	12.13	113.7
SD		0.168	
CV		1.39%	

Fig. 4: TC analysis of sample 2 (sludge after the filter press)



TIME [min]

SAMPLE# 2 IC
[x 1, C# 11, DENSITY 1.0mg/µl]

#	AREA	%	AMNT(mg)
1-	8904	1.555	26.20
2	5741	1.007	26.10
3	3832	0.987	17.80
4	7309	1.055	31.70
MN	5627	1.017	25.20
SD		0.035	
CV		3.45%	

Fig. 5: Analysis of inorganic carbon in sample 2 before homogenizing

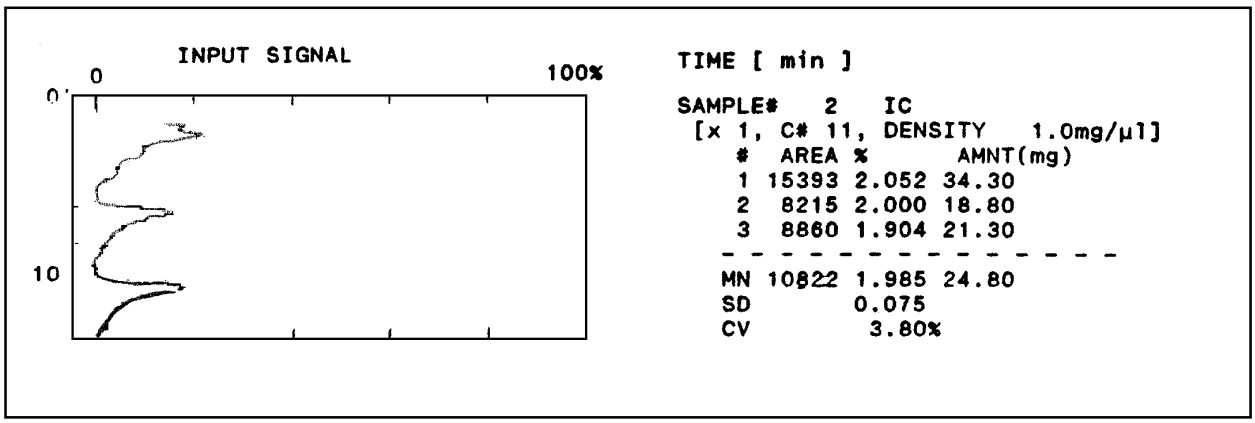


Fig. 6: Analysis of the inorganic carbon in sample 2 after homogenizing

Because of the described observations, sludge 1 after the filter press was cut up in a mortar until a homogeneously fine sample grain was available. A further IC analysis was done afterwards (shown in figure 6) . The effect of homogenizing is to be recognized distinctively. The result of the analysis for the inorganic content of this sample shows that the mean value of approx. 1% carbon almost doubled to 1,99 ± 0,08% of inorganic carbon. The peak forms show a fast increase of CO_2 concentration and it is distinctively to be recognized that the conversion is complete within the detection time.

Sample	TC
Original sludge 1	1,31 ± 0,(
Sludge 1 after filter press	12,1 ± 0,:
Sludge 1 after thermal drying	6,26 ± 0,(
Original sludge 2	1,52 ± 0,(

Table 1: sample contents in %

The results of the investigations are summarized in Table 1. As to be expected, the original sludge's show the smallest TOC content because of their considerably high content of water. If the water is removed with the filter press the TOC content in sludge 1 increases to 10,1 %. High volatile organic compounds will be removed during the thermal drying as well as the water. So that the TOC content decreases even more, compared to the pretreatment with the filter press.

Reference of Literature

/1/ MURL-Ministerium für Umwelt, Raumordnung und Landwirtschaft des Landes NRW Technische Anleitung (TA) Siedlungsabfall - Argumente und Informationen, Fakten, Daten, Zahlen, ökologische Abfallwirtschaft 12, 1993

/2/ Diplomarbeit von Dang, Thi Mai Lien über Optimierung der Bestimmung des organisch gebundenen Kohlenstoffes (TOC) in Feststoffen mit Hilfe verschiedener Meßmethoden und Analysengeräte, Fachhochschule Aachen, Abteilung Jülich

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