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THE MERITS OF THE HIGH-TEMPERATURE COMBUSTION METHOD FOR DETERMINING THE AMOUNT OF NATURAL ORGANIC CARBON IN SURFACE FRESHWATER SAMPLES

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The merits of the method for the quantitative analysis of carbon of natural organic matter (NOM) in aquatic freshwater samples, using the high-temperature catalytic combustion technique, have to our knowledge not previously been documented. Although a large intercalibration study concerning marine NOM have documented and improved the analytical merits of this technique in marine chemistry, these results cannot directly be adapted to freshwater analysis. This article presents the findings from an intercalibration on the determination of carbon in freshwater NOM, between 25 laboratories participated in using the high-temperature catalytic combustion technique. The laboratories analysed the amount of total- and dissolved organic carbon (i.e. TOC and DOC, respectively) on a set of 10 samples. The samples consisted of fresh surface water, reverse osmosis (RO) isolates of dissolved NOM from natural freshwater locations, as well as synthetic standards. General merits (i.e. accuracy, precision etc.) of the analytical method are presented and problems with detection limits, high blank values, contamination from filters, experience in the use of RO-isolates and analysis of the more refractory (i.e. not readily oxidizable) NOM are discussed. The focus of the study is on the analytical merits achieved on the natural samples compared to the commonly used and possibly readily oxidizable standard material (i.e. potassium hydrogen phthalate). It is demonstrated that the method's merits generated using the readily oxidizable potassium hydrogen phthalate are too optimistic when applied to the analysis of natural aquatic samples.

Keywords: TOC; NOM; Freshwater; RO-isolates; High-temperature combustion; Intercalibration

INTRODUCTION

Problems with poor accuracy and precision in the analysis of organic carbon (OC) have been reported in several articles concerning both the marine- and freshwater environment [1–5]. This situation has improved in recent years, as analytical instruments using high-temperature combustion and IR detection of CO₂, have become commercially available [6–8]. However, these instruments were originally developed for the determination of the amount of carbon in samples from oil refineries. The carbon analysis of natural organic matter (NOM) in water samples is today routinely

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determined using the operationally defined method intended for water samples contaminated with oil; i.e. nonpurgeable organic carbon (NPOC). Although applicable also to natural samples, the merits from manufactures do not necessarily reflect the analyte and matrix in natural aquatic samples.

Marine chemists have during the last decade documented and improved their analytical merits with great success [3–6,8]. These achievements can however likely not be directly applied on freshwater NOM analysis, due to the structural difference of the freshwater NOM [9] and difference in concentration range from that of marine NOM [1,10]. These factors cause the use of different high-temperature catalytic combustion material. Furthermore, the sample matrixes differ greatly between the two environmental systems.

A major concern in the analysis of freshwater NOM is the recalcitrant nature of this material [1]. Potassium hydrogen phthalate is the common standard reference material prescribed by the International organization for standardization (ISO) [11]. Because of its smaller size (MW 204.23 g/mol) and simple structure compared to average NOM, we hypothesize that it is likely to be easier to combust and thereby detect by these instruments than NOM. Method's merits generated using potassium hydrogen phthalate, may therefore not give a true picture of the method's ability to detect all of the more refractory fractions of NOM.

Standard reverse osmosis (RO) isolates from natural freshwater provides OC in a form that is easy to transport, store and handle, and which can provide samples with a controlled amount of OC. These materials have recently been made commercially available through the International Humic Substance Society [12]. To our knowledge, no interlaboratory comparisons concentrating on this method for determining of dissolved organic carbon (DOC) in natural freshwaters and emphasising these potential problems have been published. An intercalibration determining OC on a set of 10 freshwater samples was therefore conducted in August 1999.

EXPERIMENTAL

Apparatus

A general overview of brand, type, and age of the instruments applied in the intercalibration is presented in Table I.

In all of the instruments the OC is combusted to CO₂ by means of high-temperature and catalysis. The CO₂ is subsequently detected using an IR detector. Combustion temperature varied from 680 to 900°C. Platinum, and in some cases palladium, is

TABLE I The brand, type, and age of the instruments used by the laboratories participating in the intercalibration

| <i>Number of instruments</i> | <i>Commercial name of instruments</i> | <i>Purchase year</i> |
|------------------------------|---------------------------------------|----------------------|
| 2 | Astro 2100 | 1996 |
| 4 | Dohrman DC-190 | 1991–1994 |
| 1 | Shimadzu TOC 500 | 1985 |
| 11 | Shimadzu TOC 5000 | 1990–1999 |
| 5 | Shimadzu TOC 5000A | 1995–1998 |
| 1 | Shimadzu TOC 5050A | 1998 |
| 1 | Not specified | – |

used as the catalytic material. Most of these instruments can be equipped with catalyst material of different sensitivity. A high sensitivity catalyst typically provides reproducible results well below 1 mg/L and would probably be the natural choice for marine NOM analysis with concentrations seldom exceeding 2 mg/L. The concentrations normally found in freshwater, would soon devour this catalyst. The freshwater chemistry environment is therefore limited to a less sensitive catalytic material with higher capacity, which is suitable for analysis above 4–5 mg/L, and has a reliable detection limit in the area of 1 mg/L [13].

The reactor chamber varied in size and geometry, with a length from 8 to 44 cm and diameter 4 to 22 mm, placed vertical or horizontal in the instrument. The carrier gas was either synthetic air or O₂.

Intercalibration Samples

The intention of this intercalibration was to reveal problems when determining the amount of carbon of NOM in freshwaters using high-temperature combustion TOC analysers. The intercalibration samples should therefore satisfy the following requirements:

- A. Certified concentration for accuracy determination
- B. Nonlabile material in order to assure no change during sampling and handling
- C. Contain not readily oxidizable material in order to reveal inadequate ability to combust all fractions of NOM
- D. Cover the range in total organic carbon (TOC) and matrixes commonly encountered in natural samples
- E. Low concentration in order to reveal detection limit and high blank value problems
- F. Mix of organic and inorganic carbon in order to reveal deviations that can arise by the use of various techniques in determining total carbon (TC), total inorganic carbon (TIC) and TOC

The samples that were used for the intercalibration are presented in Table II. The intercalibration results of the combination of these 11 samples were found to be well suited for discussion of problems associated with the determination of carbon in NOM found in freshwater locations.

TABLE II Description of the samples used in the intercalibration. The letters in the purpose column refer to the list of requirements stated above

| <i>Sample type</i> | | <i>Description</i> | <i>Purpose</i> | <i>mg CL⁻¹</i> |
|----------------------|----|---|----------------|---------------------------|
| RO-isolated Na-salts | 1 | The Nordic reference NOM | A, B | 9.4 |
| | 2 | Hellerudmyra (Spring), Eastern Norway | B, D | 18 |
| | 3 | Lake Maridalsvann, Eastern Norway | B, C | 2.7 |
| Fresh natural water | 4 | Lake Hietajärvi, Eastern Finland | C, D | 4.1 |
| | 5 | Svartberget, Northern Sweden | D | 15 |
| | 6 | Birkenes, Southernmost Norway | D | 8.0 |
| Synthetic standards | 7 | Potassium hydrogen phthalate | A, E | 0.5 |
| | 8 | Potassium-bicarbonate and -hydrogen phthalate | A, F | 9.0 |
| | 9 | Potassium hydrogen phthalate | A | 9.0 |
| | 10 | Cu-phthalocyanime-tetrasulfonic acid | A, C | 9.0 |
| | 11 | Local carbon free water | E | 0 |

The purpose of the nonlabile RO material, in addition to fresh samples, was to rule out the possibility of changes in the OC amount during transport and handling as a cause for deviating results. The RO isolates are made from runoff or lake water. First the NOM is up-concentrated about 50 times using a RO technique [14,15]. The concentrate is further rota-evaporated and finally freeze-dried. Intercalibration Sample 1 is a *Nordic NOM-reference material* [16]. In addition, two well-studied isolates were selected [11]. A spring sample isolated from the bog *Hellerudmyra* was chosen due to its high concentration of fresh organic matter and an isolate from *Lake Maridalsvann*, which is a large lake (3.9 km²), was selected as it consists of refractory material [17]. The Nordic NOM-reference material is now commercially available through the International Humic Substance Society [12]. Aliquots of the RO-isolates were prepared by weighing out an accurately determined amount into sealed glass ampoules. The participating laboratories prepared the Samples 1 to 3 by dissolving quantitatively each isolate in their carbon free water to 100 mL. The participants were provided with dedicated filtering equipment (Millipore MILLEX-HA nonpyrogenic sterile 0.45 µm filter cartridge using a 5 mL syringe) for the RO-isolates in order to distinguish loss in precision due to the filtering step from measurement errors in the data set. The participants were informed how to rinse these filters prior to filtration to avoid contamination.

The fresh natural water samples (intercalibration Sample 4,5, and 6) were collected from stream or lake water in three of the Nordic catchments studied in the NOMiNiC project [17]. These catchments are thoroughly studied sites in Finland, Sweden, and Norway. The sites are the UN-ECE ICP-IM sites Hietajärvi [18,19] in North Karelen or Finland, Birkenes [20] in Southernmost Norway and the Svartberget site in Northern Sweden [21,22]. The samples differ in the quality and quantity of NOM and in matrix composition. Hietajärvi is a large lake (1.12 km²) probably causing the sample to consist of NOM with a high degree of refractory material in a high pH environment. The sample from Svartberget, which is dystrophic stream draining a bog, has a high total NOM concentration and consists of less complex but relatively hydrophobic humic material. Finally the Birkenes sample is from an anthropogenically acidified site with low pH and high ionic strength.

In order to minimize changes in the amount of TOC during shipment and handling the bulk samples were all filtered using a ~0.7 µm prebaked Whatman glass microfiber filter (GF/F 47 mmØ) prior to shipment to the participants. The participants were instructed to store the samples cool and conduct the analyses for TOC, DOC, and DIC within a week using their own filtering equipment to define the cut-off between TOC and DOC and their own method for DIC determination.

The synthetic Samples 7 to 9 were prepared from potassium hydrogen phthalate, which is the most commonly used material for preparing OC standards. The Cu-phthalocyanime-tetrasulfonic acid used to prepare Sample 10 is a very refractory material and considered to be more challenging to combust. Both materials used in the synthetic samples are also used in the ISO standard for the determination of TOC and DOC [11].

The sets of water samples (no. 4–7) and standards (no. 8–10) were distributed in prebaked brown glass bottles with teflon-lined caps using express-mail. The individual laboratories were requested to prepare and determine their carbon free water, which is the 11th sample.

Analyses of DOC on 3 replicates of Samples 1–6 and TOC in Samples 4–11 were then conducted within a week after receiving the intercalibration samples. The participants were encouraged to use their laboratories own normal procedures regarding filtering, conserving and standards.

The laboratories were also requested to report their blank values. All samples and a sample of the blank water from the laboratories were returned to the University of Oslo and reanalysed in order to reveal any sample distortion during handling, transportation, and analysis. UV absorption by spectrophotometer was also performed to support the reanalysis with an alternative method, and thereby detect and rule out sample distortion, gross errors and confirm the concentrations of the RO-isolate solutions.

RESULTS AND DISCUSSION

In order to identify outliers and significant differences between the accuracy and precision of the method and participating laboratories, various statistical methods, both assuming normal distribution (*T*-tests, Two-way ANOVA) and a nonparametrical ranking method, have been applied.

General Precision and Accuracy

The reanalysis at UiO of Samples 4–11 at the end of the intercalibration period revealed no significant changes in the OC content. No detectable distortion of the samples due to transport storage or handling occurred for the duration of the intercalibration period. UV-absorption measurements confirm this conclusion. This could be interpreted as any possible changes to the samples happened prior to the shipment to the participants, and that the samples were fairly stable after any initial changes. Sampling techniques and possible changes occurring between field and laboratory, are however not included in this investigation.

Average, median, and standard deviation were established for each of the intercalibration samples, Table III summarizes the general statistics for the analysis of the 10 intercalibration samples. The absolute standard deviation (STD) between the laboratories varied from 0.3 to 1.4 mgCL⁻¹ for the different intercalibration samples.

TABLE III General statistics of the intercalibration results. Numbers 1–10 refer to the intercalibration samples described in Table II. Values are given with the denomination mgCL⁻¹. Outliers at 95% significance level are removed from the general statistics

| | <i>RO-isolates</i> | | | <i>Fresh natural samples</i> | | | | | | <i>Synthetic standards</i> | | | | <i>Blank</i> |
|----------|--------------------|-----|------|------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------------------|------|------|-----|------------------|
| | 1 <i>DOC</i> | 2 | 3 | 4 <i>TOC</i> | 4 <i>DOC</i> | 5 <i>TOC</i> | 5 <i>DOC</i> | 6 <i>TOC</i> | 6 <i>DOC</i> | 7 <i>TOC</i> | 8 | 9 | 10 | 11 <i>TOC</i> |
| MEDIAN | 8.6 | 17 | 3.0 | 4.2 | 4.1 | 15 | 15 | 8.1 | 4.1 | 0.7 | 4.7 | 9.0 | 11 | 0.1 |
| MAX | 9.6 | 19 | 3.8 | 5.5 | 6.2 | 17 | 17 | 8.8 | 6.2 | 1.2 | 6.0 | 9.6 | 13 | 0.8 |
| MIN | 7.0 | 13 | 2.4 | 3.1 | 3.1 | 12 | 13 | 6.9 | 3.1 | 0.0 | 2.8 | 8.2 | 9 | -0.1 |
| Outliers | 1 | 1 | 2 | 0 | 1 | 2 | 2 | 2 | 1 | 0 | 1 | 0 | 2 | - |
| AVG | 8.5 | 17 | 3.1 | 4.3 | 4.2 | 15 | 15 | 8.0 | 4.2 | 0.7 | 4.8 | 8.9 | 11 | 0.1 |
| STD | 0.71 | 1.3 | 0.38 | 0.61 | 0.70 | 1.2 | 1.4 | 0.48 | 0.70 | 0.27 | 0.62 | 0.41 | 1.3 | - |
| SDT% | 8.4 | 7.3 | 12.5 | 14.3 | 16.4 | 8.2 | 9.5 | 6.0 | 16.4 | 38.8 | 13.1 | 4.6 | 11 | - |
| <i>N</i> | 24 | 23 | 22 | 25 | 23 | 23 | 22 | 23 | 23 | 23 | 24 | 25 | 23 | 18 |

The deviation between the three replicates of each laboratory was nearly one order of magnitude smaller, ranging from 0.08 to 0.2 mg CL⁻¹. Relative standard deviation (% STD) between the laboratories was found to vary from 5 to 16%, except for the synthetic standard containing only detection limit levels of TOC (i.e. no. 7; 39%). This concludes that the STD is neither constant over the given concentration range (0.5–17 mg CL⁻¹), nor that it easily can be given as a fixed relative standard deviation proportional to the sample concentration.

Samples with concentrations near the level of detection showed a tendency to be overestimated. Materials believed to be not readily oxidizable, i.e. Sample 3, 4, and 10, showed the highest variance while the samples based on the most common standard material in the artificial Sample 9, the likely more readily oxidizable potassium hydrogen phthalate, were reproduced with greater certainty.

The filtering step from TOC to DOC increased the standard deviation, in regards to both the intra- and interlaboratory precision. On average the precision of the laboratories decreased with 0.01–0.05 mg CL⁻¹ while the variation between the laboratories increased with 0.1–0.3 mg CL⁻¹.

Outliers were detected at 95 and 99% significance both using Students *T*-test and the Dixon *Q*-test. The 95% significance test should be interpreted with care since statistically one of twenty results will lie outside the 2.5% borders. In our population of 25 it is therefore likely that the value from one laboratory lies outside the borders for random reasons. However, it is not likely that the same laboratory is represented several times in this range. Some of the laboratories were overrepresented in the number of outliers. A Two-way ANOVA test on the results showed that a group of laboratories got systematically significantly ($p = 0.05$) lower results than the rest.

A theoretical "true value" based on the gravimetric preparation exists for the three RO-isolates and the synthetic standards. It was therefore possible to use a student *T*-test to determine whether the group average was significantly different from the theoretical value (Table IV).

Since the data are not normally distributed, a nonparametric ranking test was performed. The OC results on each sample were sorted and the laboratories were given a ranking number for every sample according to their sequence in an increasing concentration order. If the differences in results are caused by random errors, the sum of ranks should be normally distributed around a middle value of 117 (i.e. $\text{min} = 1 \times 9 = 9$, $\text{max} = 25 \times 9 = 225$, $\text{middle} = (\text{max} - \text{min})/2 + \text{min} = (225 - 9)/2 + 9 = 117$). This analysis confirmed the results of the ANOVA test discussed above.

TABLE IV Comparison of group average with theoretical value. Values are given with the denomination mg CL⁻¹. Outliers at 95% significance level are removed from the average

| Sample parameter | RO-isolates | | | Synthetic standards | | | |
|--|-------------|----------|----------|---------------------|----------|----------|-----------|
| | 1 DOC | 2 DOC | 3 DOC | 7 TOC | 8 TOC | 9 TOC | 10 TOC |
| Theoretical value | 9.4 | 17.7 | 2.7 | 0.5 | 4.5 | 9.0 | 9.0 |
| AVG | 8.5 | 16.9 | 3.1 | 0.7 | 4.8 | 8.9 | 11.0 |
| Significant different at 95% level (students <i>T</i> -test) | | | | | | | |
| AVG too low | Yes | | | | | | |
| AVG too high | | | Yes | Yes | | | Yes |

The various methodical factors (i.e. reaction temperature, oxidative catalytic material, geometry of the reactor chamber, and carrier gas) were sorted according to their rendered carbon concentration. This analysis revealed that the only coherent difference between laboratories with systematic too low estimates and the rest of the participants was that the reactor chamber in their instrument was placed horizontally instead of vertically. To our surprise, raising the reactor temperatures from 680 to 900°C did not appear to have any influence on the results. Furthermore, the underestimation of OC by the instruments with horizontal reactor chamber varied, being low for the readily oxidizable artificial standards based on potassium hydrogen phthalate and very high for less readily oxidizable NOM and Cu-phthalocyanime-tetrasulfonic acid (Sample 10). For not readily oxidizable material the errors were unacceptably large. Some of the participants detected only 30% of the DOC present in the sample. A horizontal reactor tube may serve as a reasonable cause for these problems, since a longer lifetime of refractory organic molecules in the reactor tube may allow the sample to fall down and become unevenly distributed on along the reactor wall. Users of this type of instrument have also noted a problem of tailing of the peaks on their CO₂ detection curves, which is consistent with this hypothesis.

Detection Limit and Quality of the DOC Free Water

The laboratories reported limits of detection (LOD) in the range 0.05–2.0 mg CL⁻¹ with 0.5 mg CL⁻¹ as the most reported value. Intercalibration sample no. 7 (0.5 mg CL⁻¹ KH-phthalate) was designed in order to investigate the concentration range near the common LOD. Two laboratories reported the TOC level to be below their LOD (0.5 and 2.0 mg CL⁻¹) and the rest reported values between 0.00 and 1.17 with an average of 0.69 and a standard deviation of near 40%. DOC concentrations close to the detection levels were most likely to be overestimated. The intralaboratory relative standard deviation on this sample (i.e. within the tree replicates) varied from about 1% to over 50%. There is however no consistency between the laboratories with low reported LOD and the lowest standard deviation. Intercalibration standard no. 3, containing a low OC concentration (2.7 mg CL⁻¹) of NOM, was found to be significantly overestimated and showed a high relative standard deviation around 15%. It is therefore reason to be concerned that some reported LOD are too optimistic, and laboratories frequently analyzing freshwater in this sensitivity range are encouraged to frequently monitor the LOD of their instruments using the IUPAC definition LOD; i.e. three times the standard deviation of the blank signal. Laboratories using instrument with several sensitivity ranges should also keep in mind at what range they are operating and that each sensitivity range corresponds to a specific LOD. Since the oxidation and combustion can be less effective for some natural organic material than for potassium hydrogen phthalate, the laboratories are further encouraged to document and monitor their analytic performance on samples containing real NOM in low concentrations (accuracy and precision). To achieve this, we recommend the use of stable RO-isolates as a tool for the documentation of analytical merits.

23 of the 25 laboratories reported the TOC levels of their blanks. 5 reported the TOC level to be below their LOD (0.4–2.0 mg CL⁻¹). The rest of the laboratories found blank values between 0.0 and 0.8 mg CL⁻¹, which with a few exceptions, were below their reported LOD. Detection limit calculated according to the method described in [23] (i.e. $LOD = t\text{-value} (p = 0.01, N = 16) \cdot \text{std of blank values from all the laboratories}$)

is 0.60 mg CL^{-1} . This estimates LOD is based on a routine with three replicate measurements on each sample. The general impression is that the quality of the blanks was good, but there should be consistency between the reported LOD and quality of the blank water samples for a laboratory.

DOC Analysis and Contamination from Filters

Contamination from the filters, used to separate DOC from particulate organic carbon (POC), was one of the potential problems that the set of intercalibration samples was designed to reveal. Since the participants were requested to determine both TOC and DOC in the three freshwater samples (no. 4–6), containing only minor amounts of POC, and in their own blank, it was possible to disclose several potential cases of filter contamination. To prepare the sample for DOC analysis, the POC was removed by filtration. The laboratories were asked to use the brand of filter and pore size they use in their standard procedure. 16 laboratories used filters with a pore size of $0.40\text{--}0.45 \mu\text{m}$. Two used pore size $0.70 \mu\text{m}$ and three used $0.20\text{--}0.22 \mu\text{m}$. There was found an insignificant increase in the reported DOC concentration with increasing pore size of the filters used to separate DOC from TOC. The small difference is probably mainly due to the minor POC fraction in these samples. Furthermore, no significant differences were found between the different types or brands of the filters used by the laboratories. The sample preparation step from TOC to DOC caused both inter- and intralaboratory precision to decrease. On average the intralaboratory precision decreased with $0.01\text{--}0.05 \text{ mg CL}^{-1}$, while the interlaboratory precision decreased with $0.1\text{--}0.3 \text{ mg CL}^{-1}$. Eleven laboratories displayed DOC values more than one standard deviation higher than their reported TOC values. 5 laboratories consistently reported DOC values more than 5% higher than their TOC value. The average level of contamination in this group was about 1 mg CL^{-1} and in some cases more than 3 mg CL^{-1} , which is far above their standard deviation for these samples.

11 laboratories reported both TOC and DOC on their blank water. Five laboratories reported more than twice the amount of DOC as TOC (with 0.4 mg CL^{-1} difference or more). There was a consistency between those having contamination in the natural samples and in their blanks. Again no significant differences were disclosed among the different filter materials, although cellulose filters seem to be more prone to give too high DOC values.

Analytical Merits on NOM Compared to Readily Oxidizable Standards

A Youden analysis [23,24] plot (Figs. 1 and 2) of the intercalibration data provides a clear illustration for most of the essential features found in this intercalibration. The individual results were normalized by dividing with the average result or, when known, the actual concentration, and subtracting 1.

A systematic trend ($r^2 = 0.38$) in the over- and underestimation of OC was revealed when results for TOC and DOC from each sample and laboratory were compared in a Youden plot (Fig. 1). A few laboratories significantly and systematically underestimate the amount of OC, especially for samples with high TOC concentrations and refractory material. The laboratories reporting the lowest values all had TOC instruments where the reactor column is oriented horizontally instead of vertically. Laboratories showing overestimation of DOC, though combined with

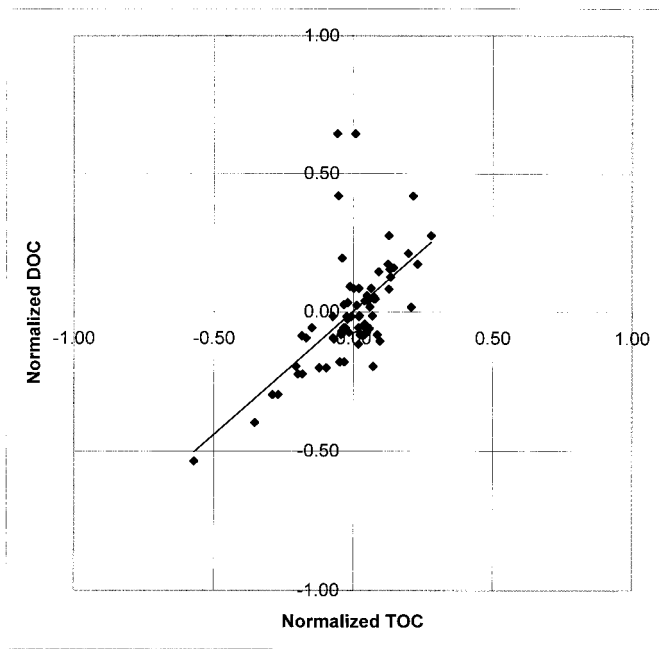


FIGURE 1 Youden plot of normalized TOC and DOC results from each sample and laboratory.

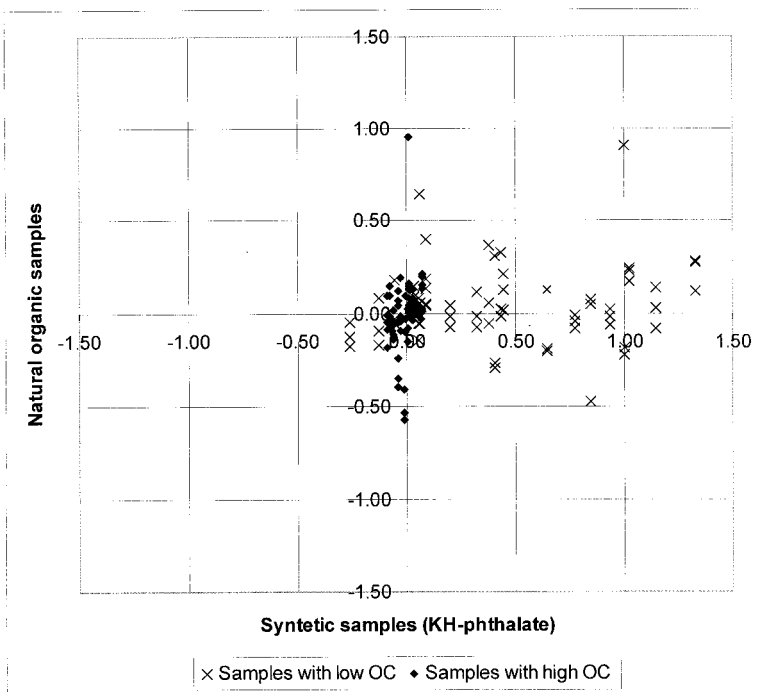


FIGURE 2 Normalized results from the analysis of natural samples with high or low level of organic carbon (OC) compared with normalized results from the analysis of synthetic samples (intercalibration Sample 7 and 9).

very high accuracy for TOC, are likely experiencing contamination problems caused by the filter.

Other important features are illustrated by comparing the results from the natural samples with results from the more readily oxidizable samples of similar OC levels (Fig. 2). The 0.5 mg C L^{-1} synthetic standard (no. 7) is generally strongly overestimated illustrating the detection limit and filter contamination problems. The standard deviations of the more readily oxidizable 9.0 mg C L^{-1} standard (i.e., no. 9: potassium hydrogen phthalate), generally applied to prepare calibration standards, are significantly lower than the standard deviation of the natural samples with similar amount of OC. This should be born in mind when such solutions are used to generate the method's merits.

CONCLUSIONS

The general accuracy of the laboratories was found to be 0.3 to 1.8 mg C L^{-1} . The precision was nearly one order of magnitude smaller, from 0.08 to 0.2 mg C L^{-1} . Accuracy and precision were high for the typical readily oxidizable standard material, but decreased for natural aquatic samples containing less readily oxidizable NOM. This was especially the case for the instrument with horizontal reaction tube. Higher reactor temperature did not influence significantly on the results.

DOC concentrations close to the detection limit were most likely to be overestimated. The laboratories reported LODs from 2.0 mg C L^{-1} down to 0.05 mg C L^{-1} , which turned out to be too low in some cases. Statistical computation of LOD from the blank results of the laboratories suggests 0.60 mg C L^{-1} to be a reasonable detection limit based on potassium hydrogen phthalate, but this may be too optimistic if applied to analysis of not readily oxidizable NOM. Cu-phthalocyanime-tetrasulfonic acid was the least readily oxidizable of all the samples and providing the most pessimistic estimate of the analytical performance. Analytical performance for samples based on NOM (i.e. freshwater and RO-isolates) were found to be in between these two extremes. Laboratories analyzing NOM are therefore encouraged to document their detection limit, accuracy, and precision using standard natural material like RO-isolates.

The results of this intercalibration emphasise the need for a standard procedure for laboratories analyzing NOM from freshwater systems on high temperature catalytic combustion instruments, in order to be able to discuss and compare their results in a reliable way.

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