

## Intercalibration of Gas Chromatographic Analyses for Hydrocarbons in Tissues and Extracts of Marine Organisms

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Gas chromatographic analyses of hydrocarbons separated from tuna meal samples and cod liver lipid extracts have been intercalibrated among three laboratories. Measurement of petroleum hydrocarbons spiked to samples of cod liver oil gave values as follows:  $\bar{x}$ ,  $(\bar{x} - \bar{x})/\bar{x}$ ,  $s/\bar{x}$ ; distillate cut of South Louisiana crude oil—372  $\mu\text{g/g}$ , 0.09, 0.06; No. 2 fuel oil—1163  $\mu\text{g/g}$ , 0.50, 0.26; Wilmington crude oil—913  $\mu\text{g/g}$ , 0.69, 0.34. The estimates of petroleum hydrocarbons in tuna meal subsamples gave  $\bar{x} \pm s$  of  $37.7 \pm 4.6$   $\mu\text{g/g}$  dry weight. Measurements of pristane in cod liver lipid samples gave  $\bar{x} \pm s$  of  $35.7 \pm 3.5$   $\mu\text{g/g}$  lipid and  $271 \pm 4.5$   $\mu\text{g/g}$  lipid. Measurements of pristane in tuna meal were less precise with  $\bar{x} \pm s$  of  $2.4 \pm 1.5$   $\mu\text{g/g}$  dry weight. Some limitations to current methods of analysis as applied in this study and in several current oil pollution studies are demonstrated and discussed.

These studies will require the efforts of many laboratories throughout the world because of the complexity and global nature of the oil pollution problem. This is already apparent to some degree in the oil pollution research literature.

An important factor in field or laboratory studies is the precision, accuracy, and intercomparability of the data gathered using the same or different methods of analyses in different laboratories (1-3). We initiated a program of intercalibration between our laboratories in 1971 as part of a study program to identify problems related to oceanic environmental quality under the auspices of the Office for the International Decade of Ocean Exploration, National Science Foundation. Three laboratories were involved in studying the distribution of hydrocarbons in the biota, water, air-sea interface and sediments of the North Atlantic Ocean. Unfortunately, suitable samples for intercalibration were not

# ICES/IOC Intercomparison Exercise on the Determination of Petroleum Hydrocarbons in Biological Tissues (mussel homogenate)

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A homogenate was prepared from approximately 4000 *Mytilus edulis* sampled near the municipal sewer outfall of Boston, Massachusetts, USA. Subsamples were placed in jars. Then a set of subsamples were freeze-dried. Both wet homogenate and freeze-dried homogenate samples were checked for non-homogeneity by analyses of randomly selected subsamples by the WHOI coordinating laboratory. Three randomly selected freeze-dried subsamples were distributed to each of 50 participating laboratories from 24 countries.

Twenty-two laboratories reported UV-fluorescence data giving  $\bar{x}=24 \times 10^{-6}$  g chrysene equivalents  $\text{g}^{-1}$  dry wt  $\pm 24 \times 10^{-6}$  g  $\text{g}^{-1}$  dry wt for a  $\pm 100\%$  r.s.d. Twenty laboratories reported UV-fluorescence data in Arabian Light Crude Oil equivalents;  $\bar{x}=235 \times 10^{-6}$  g  $\text{g}^{-1}$  dry wt  $\pm 234$  for a  $\pm 98\%$  r.s.d. Between 22 and 30 laboratories reported data for n-alkanes, pristane and phytane determined by GC analyses giving between  $\pm 69\%$  and  $\pm 297\%$  r.s.d. depending on the compound. Elimination of outliers reduced the range of r.s.d.'s to  $\pm 67$  to  $\pm 104\%$  r.s.d. A similar experience was noted for data for individual polynuclear aromatic hydrocarbons

carbons in samples of the marine environment has been recognized for many years (Farrington & Teal, 1972; Farrington *et al.*, 1976; NAS, 1975; Wise *et al.*, 1980). Recent efforts have shown considerable improvement in the agreement between laboratories for measurements of selected hydrocarbons in sediments (MacLeod *et al.*, 1982) and marine tissue samples (Galloway *et al.*, 1983). However, there is much work yet to be done before analysts can be satisfied with the precision and accuracy of these measurements within and among laboratories as noted in these two latter references.

The International Council for the Exploration of the Sea (ICES) conducted an intercomparison exercise in 1980-81 which compared the data for measurements of hydrocarbons in crude oil, sediments and marine tissues (Law & Portmann, 1980). The results for both sediments and tissues revealed substantial disagreement for many of the parameters measured. Also only five laboratories reported data for the mussel (*Mytilus edulis*) homogenate tissue sample. Accordingly, the Marine Chemistry Working Group of ICES organized a

# Dissolved/dispersed Hydrocarbons, Tarballs and the Surface Microlayer: Experiences from an IOC/UNEP Workshop in Bermuda, December, 1984

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An intercomparison exercise was conducted at the Bermuda Biological Station for Research, Inc, Bermuda on 1-15 December 1984. It primarily involved the testing of the IOC Manual for monitoring oil and dissolved/dispersed petroleum hydrocarbons (DDPH) in marine waters and on beaches (IOC, Manuals and Guides, No. 13). An additional exercise sought to intercompare methodologies for the collection of sea surface microlayer samples.

DDPH measurements in the inshore waters of Bermuda resulted in a mean concentration of  $0.057 \mu\text{g l}^{-1}$  of ( $n = 30$ ) chrysene equivalents with a 60% relative standard deviation (RSD). Open ocean samples yielded a mean concentration of  $0.011 \mu\text{g l}^{-1}$  ( $n = 44$ ) with a 65% RSD. These concentrations are extremely low and the results indicate that the method described in the Manual is sufficiently sensitive for the detection of 'hot spots'.

toring contamination by petroleum in the marine environment.

The operational manual for the sampling of the sea surface microlayer (IOC Manuals and Guides, No. 15), was also tested. The results indicated that this method collects reproduceable volumes of elevated concentrations of materials from the sea surface suitable at least for qualitative analyses. However, the spatial distribution and stability of surface films may render quantitative analyses less meaningful.

In order to assess the global oceanic burden of fossil fuel hydrocarbons in the marine environment, inter-comparable data needs to be collected in order to determine ranges of concentration. To this end various intercomparison exercises have been carried out to

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## ANALYTICAL EVALUATION OF LABORATORIES WISHING TO PERFORM ENVIRONMENTAL CHARACTERIZATION STUDIES

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**Abstract**—Laboratories competing to analyze bivalve mollusks under contract to the National Oceanic and Atmospheric Administration's Mussel Watch Project were required to undergo analytical tests of their ability to quantify environmental contaminants as part of the contract evaluation process. During the 1989 selection process laboratories that appeared to qualify on the basis of their written proposals were provided a gravimetrically prepared solution with "unknown" quantities of an undefined number of organic contaminants that are regularly quantified for the Mussel Watch Project. In 1994, competing laboratories were once again tested but this time using matrix materials for the quantification of both trace elements and organic contaminants. Three laboratory groups participated in the exercises. For the 1989 gravimetrically prepared solutions, all participating laboratories were able to identify the contaminants present and in all but two cases were able to report values to within  $\pm 25\%$  of the known values. In 1994, all laboratories were within the acceptance criteria for the quantification of trace elements in the homogenate sample. Analytical laboratory testing is an important first step to ensure that environmental characterization studies are successful.

**Keywords**—Quality assurance    Analytical testing    Contracts    Trace elements    Organic contaminants



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**Certified Concentration Values:** Certified values for concentrations, expressed as mass fractions, for 24 PAHs, 29 PCB congeners, and 7 chlorinated pesticides are provided in Tables 1 through 3. The certified values for the PAHs, PCB congeners, and chlorinated pesticides are based on the agreement of results obtained at NIST from two or more chemically independent analytical techniques along with results from an interlaboratory comparison study [1,2]. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST.

**Reference Concentration Values:** Reference values for concentrations, expressed as mass fractions, are provided for 44 additional PAHs (some in combination), 13 additional PCB congeners, and 2 additional chlorinated pesticides in Tables 4 to 7. A reference value for total organic carbon is provided in Table 8. Reference values are noncertified values that are the best estimate of the true value. However, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods.

**Information Concentration Values:** Information values for concentrations, expressed as mass fractions, are provided in Table 9 for carbon, hydrogen, and nitrogen. An information value is considered to be a value that will be of interest and use to the SRM user, but insufficient information is available to assess adequately the uncertainty associated with the value or only a limited number of analyses were performed.

**Expiration of Certification:** The certification of this SRM is valid until **01 March 2012**, within the measurement



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