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ANGLO-NORWEGIAN OIL PROGRAMME - INTERCALIBRATION OF ANALYTICAL METHODS

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ABSTRACT

An attempt has been made to intercalibrate the analysis of three groups of aromatic compounds present in a sample of Ekofisk crude oil using gas chromatography - mass spectography. The results are not as good as was hoped. Two possible sources of error have been identified, one instrumental and the other related to the assumptions which had to be made regarding the responses given by different compounds of the same group but of different molecular weights or isomers of the same group. Proposals are made for overcoming these difficulties. Wider participation is invited in a repeat exercise and in a similar exercise involving the simpler u/v fluorescence method of analysis.

INTRODUCTION

Oil is a complex and variable mixture of compounds and one of the major problems involved in comparing results of analyses of environmental samples for oil, done by different laboratories, is knowing how comparable the oils used as standards really were. It is well known that the overall composition of oil from one field is different from that of another. Changes also arise in the composition of the oil produced within a single oil field; these can be quite significant. If the crude oil samples are not treated and subsequently stored under identical conditions the dissimilar loss of the more volatile

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*This paper has been prepared for the information of persons attending the 66th Council Meeting. It has been prepared not as a success story, but rather as an illustration of the difficulties involved in conducting intercalibration exercises for petroleum hydrocarbons. Further work is in progress and it is hoped that the paper will stimulate discussion and encourage others to join in the work. The authors wish to draw particular attention to the need to consult them before any reference is made to this paper.

components can make the differences between oils from the same source quite substantial. Thus it will be obvious that if two laboratories use as their standards oils of either different origin or different history, they are likely to report results which will not be directly comparable.

An equally important factor is the method of analysis used to determine the quantity of oil present. The constituent compounds of oil exhibit a wide variety of chemical and physical properties and no one method of oil analysis can measure all the compounds present: each method relies on the response of a fraction of the total constituents. A wide variety of methods having different levels of sophistication can be and are used, but with the single exception of the IGOSS method of water sample analysis using u/v fluorescence (IOC/WMO, 1976) there is no single method which is used on a wide scale. Since it is only certain components of oil which are likely to harm marine organisms at low concentrations, methods have to be found by which small quantities of individual components of oil, especially those which are most likely to be harmful, can be measured. At present, the general view is that the most harmful are likely to be the aromatic hydrocarbons, and the standardization problem can be overcome by simply referring to pure standards of the compound of interest. It is not possible to relate accurately the concentration of these individual components back to the oil involved in a problem (eg in an oil spill or operational discharge) because solution of the compounds takes place to differing degrees.

Under the general framework of the ICES Working Group on Pollution Baseline and Monitoring Studies in the North Atlantic, there has been a loose co-operation between the United Kingdom and Norway on petroleum hydrocarbon programmes. In particular this has involved the Institute of Marine Research, Bergen, and the Fisheries Laboratory, Burnham-on-Crouch. In an attempt to overcome the problems of different methods of analysis both laboratories have adopted almost identical methods of analysis - a relatively simple procedure since both laboratories have available the same computerized gas chromatograph-mass spectrometer systems. In order to establish how comparable data from the two laboratories would be, arrangements were made for sub-samples of the same Ekofisk crude oil to be analyzed for three groups of aromatic compounds by both laboratories.

METHODS

A known weight of the Ekofisk crude oil was dissolved in dichloromethane, and a known weight of each of the internal standards (fluorene and anthracene) added. An aliquot of this composite solution was then analyzed by mass fragmentographic techniques as previously described (Grahl-Nielsen *et al*, 1976; Law, 1978).

The sample was introduced by means of a splitless injector into a 20 m x 0.3 mm ID glass capillary column fitted in a Finnigan 3200-6110 computerized gas chromatograph-mass spectrometer. The injection was made at room temperature, following which the temperature was raised to 100°C, and thereafter programmed to rise at 6°C min^{-1}. The mass spectrometer was used to collect data on up to four ions at a time, the computer being used to change the ions monitored, at preset times during a GC run. The ions used and the compounds which they represented were as follows:

57 alkanes	128, naphthalene	141, methyl and dimethyl naphthalenes
166, fluorene	170, tri-methyl naphthalenes	178, phenanthrene and anthracene
184, dibenzothiophene	192, methyl phenanthrenes	198, methyl dibenzothiophenes
206, methyl phenanthrenes	212, methyl dibenzothiophenes	
226, dimethyl dibenzothiophenes		

The computer was used to calculate peak areas for each set of compounds, and quantitation was obtained by comparison with the areas obtained for the known weights of internal standards. The assumption was made that the same weight of any compound generates the same total ion current in the mass spectrometer. Peak areas were corrected to the total ion current using the percentage abundance of the ion used in the mass spectrum.

RESULTS

Table 1 gives details of the standards used to calculate the concentrations of the various naphthalenes, phenanthrenes and dibenzothiophenes present, and although in five instances the compounds used were identical, in the remaining three there were differences.

The results for naphthalenes (except for naphthalene itself) agreed within 20-30%, but agreement on dibenzothiophenes, which were present at the lowest concentration, was poor. In view of the difficulties encountered, the actual results are not reproduced here but it is useful to note the probable causes of difficulty encountered. The Burnham laboratory was unable (through the intervention of the ELENI V and AMOCO CADIZ accidents) to analyse the samples immediately and about 4 months elapsed before analysis could be accomplished. Thus, even though the standard oil was stored very carefully some changes may have taken place. The fact that on the whole the Institute of Marine Research results tended to be higher than those from the Burnham laboratory suggests that this had not occurred to any significant extent. A GLC analysis of the whole oil which indicated no obvious loss of components below C12 tended to confirm this.

An investigation was however made into the errors that might be introduced by the assumption that the response given by different compounds of the same molecular weight should be the same. The compounds used were 2, 6 dimethyl naphthalene, 2, 3 dimethyl naphthalene and ethyl naphthalene. The response of these compounds per unit weight relative to fluorene, were 1.05, 1.30 and 1.56. This could certainly go a long way towards explaining the differences which were encountered for the compounds trimethylnaphthalene, methyl phenanthrene and dimethyl phenanthrene. Since the concentrations of dibenzothiophene were calculated relative to the unsubstituted compound if the responses for the different substituted dibenzothiophenes were different it could also explain the poor results achieved with this group of compounds.

In the course of running these tests the Burnham laboratory confirmed that the response factors from run to run were reproducible for the three compounds tested. However, on re-runs of the standard mix, variations substantially in excess of the standard deviations reported by the Institute of Marine Research for six replicate analyses (max 10%) were discovered. At the time of writing

(early July) no firm explanation has been found for this, but it is possible that the problem is linked to a systematic or random instrument error. This may also explain the relatively poor results achieved.

CONCLUSIONS

The intercalibration of analysis of specific compounds in a standard sample of crude oil has proved to be rather difficult. Two causes of possible error have been identified: one a possible instrumental error at one laboratory, the other associated with the assumption that all compounds of the same group and even compounds with the same molecular weight within that group, have the same total ion current per unit weight. This latter assumption, whilst essential in the absence of a full set of standards, can lead to less absolute results. Clearly it is essential that the laboratories participating in such exercises use the same compounds as standards. Steps are now in hand to ensure that this can be done for the two laboratories involved in the exercise described above.

Once this has been achieved a further attempt will be made at intercomparison using a second sample of Ekofisk crude oil. If this is successful, water sample extracts will be exchanged and further comparability tests will be conducted. Since both laboratories now also have available u/v fluorescence equipment, at the same time as the GC-MS comparison, the results obtained by the less complex u/v fluorescence method of analyses of the same samples will be compared.

In view of the problems of collecting and extracting large uncontaminated water samples and subsequently storing them unchanged, it is difficult to envisage extension to other laboratories of the oil in water extracts comparison. The exercise on oil alone could however readily be extended to other laboratories capable of any of the following: u/v fluorescence analysis; the determination of total naphthalenes, phenanthrenes and dibenzothiophenes; the quantification of the 11 separate compounds involved in the present exercise and any further compounds on which general agreement on inclusion can be reached.

This paper illustrates the problems of ensuring compatability of data from one laboratory with those from another. Since each laboratory normally reports relative to suitable standard, the results of their normal work remain valid and the data from each separate laboratory is comparable in space and time. Close comparison of data from the two laboratories should however be approached with caution.

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TABLE 1 Compounds used in quantification of naphthalenes, phenanthrenes and dibenzothiophenes

INSTITUTE OF MARINE RESEARCH, BERGEN	FISHERIES LABORATORY, BURNHAM
Naphthalene	Naphthalene
2 - methyl naphthalene	2 - methyl naphthalene
2, 3 - dimethyl naphthalene	2, 3 - dimethyl naphthalene
2, 3, 6 - trimethyl naphthalene	2, 3, 5 - trimethyl naphthalene
Phenanthrene	Phenanthrene
1, methyl phenanthrene	-
3, 6 - dimethyl phenanthrene	9, 10 - dimethyl phenanthrene
Dibenzothiophene	Dibenzothiophene