

# Protecting the North Sea: The Analytical Challenge

The following are summaries of nine of the papers presented at a Joint Meeting of the Analytical Division and the North East Region held on February 20th–21st, 1991, in the Grange Park Hotel, Willerby, Humberside.

## Analytical Difficulties in the Full Characterization of Industrial Effluents

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Currently, industrial effluents are increasingly regulated in terms of levels of relatively few components using lists such as the UK 'Red List' and the list contained in the 1990 North Sea Ministerial Declaration. For complex effluents, regulation has traditionally been based on group parameters such as biochemical oxygen demand or chemical oxygen demand. Recently, in the pulp and paper industry, restricting discharges of organically bound chlorine (AOX, EOX and POX) has been practised. The use of total organic carbon (TOC) measurements is being widely explored as a regulatory instrument.

Neither listing procedures nor group parameters can fully account for the complexity of effluents. Even with additional toxicity testing procedures, there are problems with the extrapolation of results in order to predict the effects in the wider environment. Lists contain chemicals already identified as causing problems in the environment. The prospective effort, directed towards identification of new sources of environmental chemical risk, has been unable to prevent serious problems. Even the recent identification of tributyltin compounds as priority action chemicals was retrospective to their widespread use. An increased understanding of the nature of contaminants being discharged to the North Sea is necessary, therefore, to its future protection.

### Experimental

#### Extraction and Cleanup

Modern gas chromatography–mass spectrometry (GC–MS) methods theoretically allow characterization of many, though not all, unknown elements of effluent samples. The first stage in the analysis of an environmental sample is the extraction of the analyte. The recovery of a given analyte and any modification will depend upon its properties and the extractive conditions. At this stage, GC–MS screening of the 'raw extract' may result in the isolation of over 150 peaks. Refinement of the chromatographic conditions sometimes allows further separation but it is frequently impossible to resolve samples fully. This is particularly the case if common pollutants such as oil are present in sufficient quantity to obscure minor components.

Sequential cleanups may be applied to remove many interferences; solid phase extraction is a method of preference owing to its simplicity, flexibility and low cost. High performance liquid chromatography (HPLC) is also gaining prominence as a preparative separation stage (*e.g.*, for the polynuclear aromatic hydrocarbons). The choice of cleanup method is generally somewhat subjective. Analytical methods

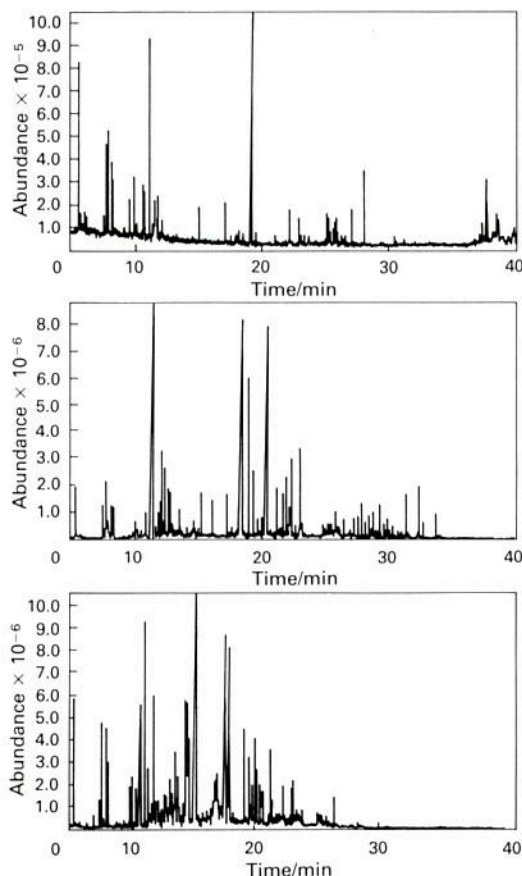


Fig. 1 Analytical traces obtained from a hexane extract of a discharge of the River Tees. These samples, taken on three separate occasions, clearly show the variability of the effluent

are naturally tailored to the removal of all but the specific target compounds. Painstaking work is required to assure accurate isolation and precise determination of a target analyte whose properties are poorly known. With this in mind, the dischargers themselves have a great contribution to make in that they will be aware of the materials in use at the time of sampling. Hence, publication of a toxic use audit, as is becoming standard in the USA, is helpful in regulation and

**Table 1** Peaks resolved under identical conditions from hexane extracts of effluent samples discharged into the Tees estuary. Peaks matched against the National Institute of Standards and Technology spectral library at the 90% and 50% level are recorded with the percentage remaining unmatched at each probability in parentheses

Sample	Industrial sector	Peaks resolved	Matched > 90% (% unmatched)	Matched > 50% (% unmatched)
A	Steel	9	4 (55.6)	4 (11.2)
B	Mixed sewage/industrial	22	3 (86.4)	13 (27.8)
C	Chemical/agrochemical	108	8 (92.6)	46 (50.0)
D	Combined chemical	30	6 (80.0)	16 (26.6)
E	Combined chemical	131	20 (84.7)	46 (49.7)
F	Combined chemical	158	36 (77.3)	79 (13.5)

enforcement activities. Even so, interactions of effluent components in mixed effluent systems producing new chemicals are not unknown.

## Results

### Identification

Once the required separation has been achieved chromatographically, the problem of identification remains. This is generally done by computer probability based matching of analytical mass spectra against library spectra. Effectively, one imperfect set of data is compared with another using an imperfect algorithm. There is a high potential for false positive and negative identifications. Where a compound is not present in the library, spectra must be evaluated by a specialist. Differing spectra, moreover, might be obtained from different types of mass spectrometers. Most of the spectra in commercial libraries were originally recorded on various instruments of the magnetic sector type and some manufacturers of other types of machines modify the spectra to compensate for this. In addition, original data are already known to be partly corrupted by artefacts and impurities in reference compounds, causing further identification problems.

Automated analyses are therefore best considered as an interpretative aid rather than a process leading to absolute identification. Currently, the analyst must rely on judgment when examining library search results in order that obvious false positive results are not reported. It is unlikely that this subjective element will be able to be completely removed from this type of work despite efforts made to do so. It is unlikely, in addition, that the library compilers can ever hope to catch up with the five million or so known organic structures, far less deal with the quantity of new chemicals produced per year, with their associated contaminants and by-products.

Retention indices may be of use in backing up the spectral matching but a suitable database has first to be established by the laboratory. It would, however, be limited to those compounds that have already been the subject of research and for which standards exist. Retention indices, furthermore, are dependent on the stationary phase used in the chromatographic column and would need to be recalculated if this were to change.

### Quantification

Full quantification is naturally impossible when dealing with analytes for which no standard is available and for which relative detector response is unknown. Semi-quantitative results may be obtained from comparison with internal standards or as a proportion of a TOC reading, if available. In either case, however, it is difficult to correct accurately for recovery and this must be accounted for when assigning uncertainty factors to results generated in this way. Inter-laboratory comparisons of analyses have shown that extensive problems exist with quantification. All in all, this adds up to the characterization of effluents being a somewhat inexact science, but one whose importance is being increasingly recognized.

### Conclusion

The work undertaken in this laboratory has largely been restricted to industrial effluent but similar problems clearly attach to other environmental media; air and sediments also present extreme analytical difficulties. Given this, the current moves by various international bodies towards a more precautionary approach to contamination of the North Sea environment, underpinned by clean production methods to reduce waste generation, must begin to look increasingly attractive to analysts and regulators alike.

## Environmental Monitoring and Analysis in the North Sea Under the North Sea Task Force

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The North Sea Task Force (NSTF) has established a harmonized international scientific programme, coordinated within their Monitoring Master Plan (MMP). The objective of this plan is to develop an adequate coverage of good quality data to allow assessment of the condition of the North Sea, and of time trends of physical, chemical and biological parameters. In the short term, the monitoring data will be incorporated into an updated Quality Status Report to be completed by 1993. Although the NSTF plan covers only the North Sea and

English Channel, the UK National Monitoring Programme will extend the coverage to include the Irish Sea, Cardigan Bay and the Bristol Channel.

The MMP incorporates a range of determinands, some of which are mandatory at all NSTF stations while others are optional. In addition the matrices to be analysed are defined for the purposes of assessing possible hazards to human health, the existing level of marine pollution, and the effectiveness of measures taken to reduce marine pollution. The main gap in