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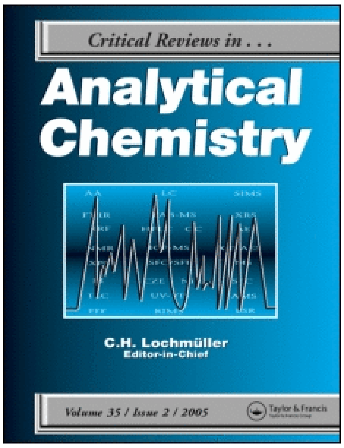

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C. H. Lochmüller; Mihkel Koel

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COST-EFFECTIVE ENVIRONMENTAL ASSESSMENT AND THE ROLE OF RESEARCH TO DEVELOP NEW TOOLS FOR MEASUREMENT

C. H. LOCHMÜLLER

**Department of Chemistry, Duke University, Durham,
North Carolina, USA**

and

MIHKEL KOEL

**Department of Analytical Chemistry, Institute of Chemistry,
Akadeemia tee 15, Tallinn EE0026, Estonia**

Introduction

There are many ways to view the important task of understanding and planning for potential and existent environmental pollution problems. Certainly the most efficient method is to build into the process – manufacturing, power generation, waste disposal, effluent water treatment – the sensing and control methods before the process is begun. That luxury does not exist in areas already subject to untold degrees of pollution from careless handling, disposal, emission or release of hazardous materials. When many problems already exist, there can arise a need to fit the schedule for remediation and control into the available fraction of the GDP that will be devoted to such efforts. Faced with limits on the amount of available resources, a strategy for ranking the problems and potential problems in some priority order seems a worthwhile tool.

In the mid 1970's in the United States the Office of Energy Minerals and Industry of the U. S. Environmental Protection Agency sought to develop both a process and a survey result they called "Environmental Assessment". The goal was to rank in a prioritized fashion ALL elements of American industry. The development of the analytical protocol for that effort required a change in the normal 'mindset'. That effort is what we would like to share first-if only in outline form. It cannot be overstressed that both measurement of source content and research on the processes themselves are important. We will draw the latter example from some work done in collaboration and related to energy production waste in the northern-most Baltic Republic.

Our goal in this paper is two-fold: A. To give an example of how a cost-effective strategy is developed and what is involved in such decisions from the view of one of the central participants {CHL}. Making the measurements that give the most information for the least total cost is a true challenge in measurement science and requires a willingness to not view everything as a primary, basic research effort or a candidate for some established, familiar and comfortable technique. The Environmental Assessment Strategy is not the only way to approach the problem of 'macro-environmental' assessment and prioritization – it is one model. It was successfully applied in programs in the USA costing hundreds of millions of dollars over a ~5 year period but is only a model. B. To show, in outline form, how research in measurement science can lead to information-rich results from a relatively low-cost experiment. The application of thermochromatography and evolving factor analysis {EFA} to studies of the geo-polymer called oil shale is a small example of how research on complex chemical systems if done well can give insights into process control planning itself. {Joint work: CHL, MK period 1985-97}

A Strategy for Environmental Assessment

Any large-scale project puts extra demands on both quality control and quality assessment efforts. In the end it is very desirable that all the data:

- Be comparable
- Be the result of use of the same protocols in every case
- Be well documented as to source, handling, storage, instrument calibration, method and operator validation.

Narrowing the focus a bit to only the sampling and determination of content stages of the entire process, what measurement techniques should be used? It is easy enough to say: " Well, all the organic determinations can be done by mass spectrometry!" or " All the inorganic content determinations can be done by atomic absorption!" All too easy to say until one realizes that the cost would be prohibitive and that some 'screening' of samples which would rank them as worthy of the expense is justified. Suppose, for example, that the site was a former air base and that the ground and water table contains tons of aircraft fuel, coal liquefaction waste and the potential for the presence of primary and hydrolyzed biocides e.g.- phosphorus – based nerve agents. Exaggerated example? Not really. The real point is that the strategy must be able to detect chemical elements of concern over the range of high percentage to at less than part-per-million. There are areas in the Baltic where it was possible for several years to obtain heating oil by digging shallow wells near former military installations and collecting jet fuel { approx. #1 diesel fuel/kerosene}. The planning for remediation of such a site would require literally hundreds of test wells and enough measurements to create a topological map of the soil/water table pollution condition of the site. If each well sample required US$1000 to collect and analyze and replicates were done a conservative cost of the first phase of measurement alone is US$300-500 000. Against that background one would need to find other, unexpected and possibly more hazardous waste elements.

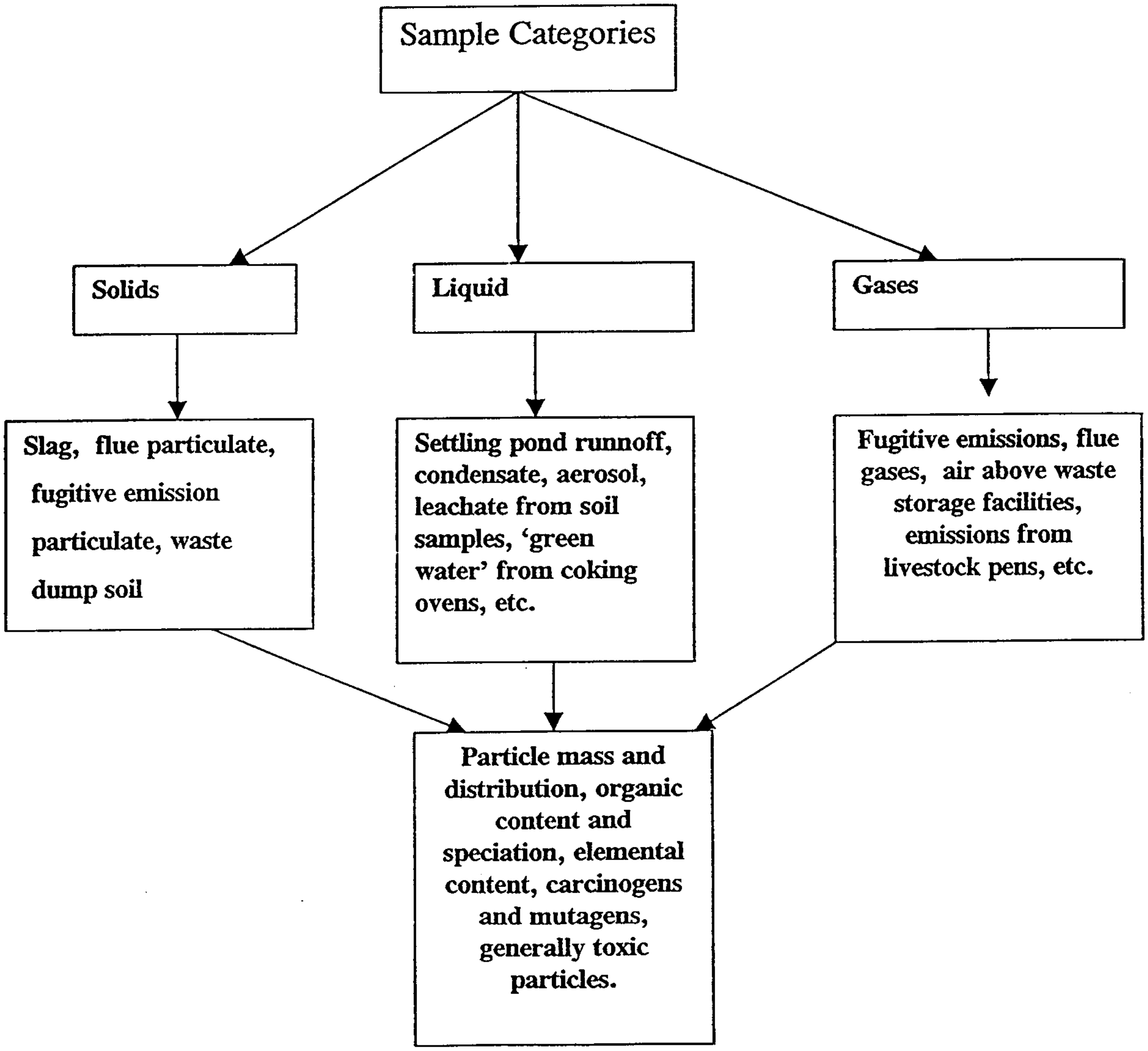
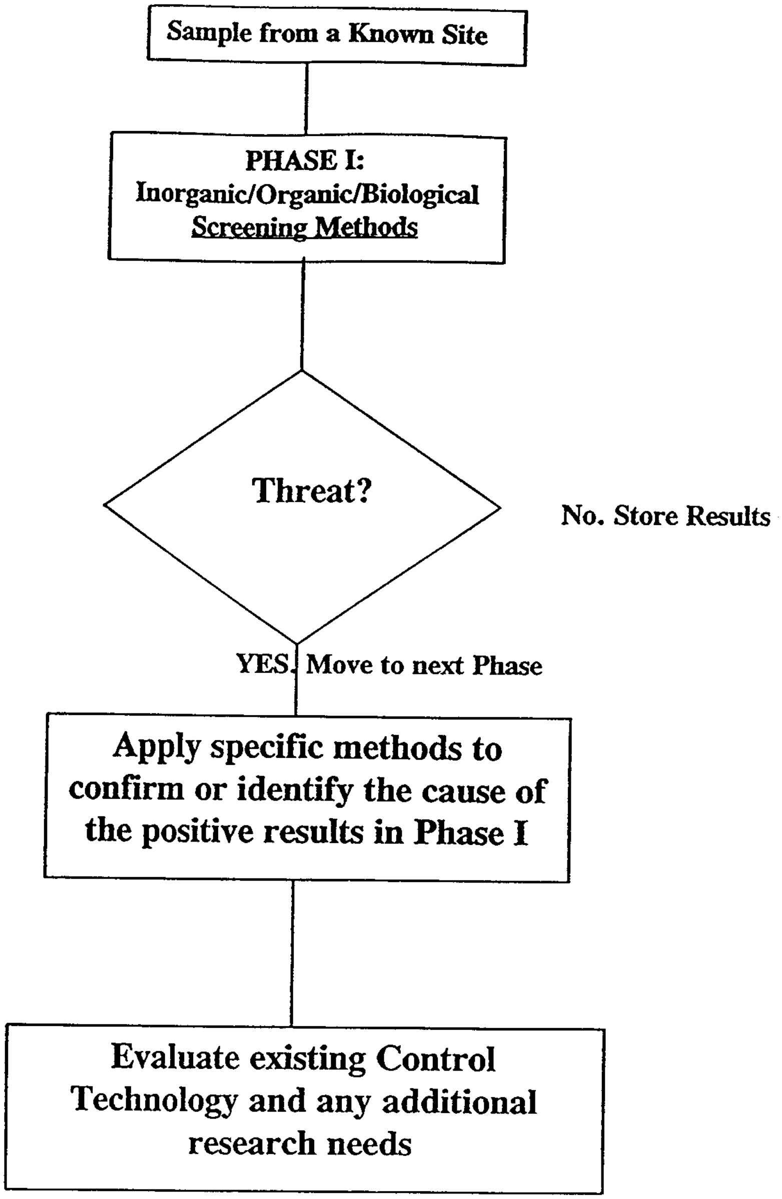


Figure 1. One way to divide the possible sample sources from industrial or military sites

The question of finding mutagens and carcinogens was troubling because the classic, whole-animal methods were not an option based on cost alone. In what was a giant-step two decades ago, we added another kind of 'analytical method' to the list or actually two: Alveolar Macrophage survival and revertance of s. typhomereum {the Ames test}. These tests could be applied to particulate solids and to extracts/leachates to give indication of risk from a different sense than the elemental or chemical class results. Collection of the amount of flue gas particulate for use in the macrophage testing, the organic and inorganic analysis methods required the design of a new kind of high-volume sampler with size segregation, vapor phase-borne organics trapping and scrubbing of the gas leaving the traps. That was achieved. What is seems more reasonable to dwell on here are the chemical characterization approaches. The methods had to be adapted to or adaptable to a wide range of samples and sample origin.

A Phased Approach

It was decided to develop a three-phase approach to sample examination. In Phase 1, the samples would be characterized well enough to direct the selection of members of the sample sets for further study in a second phase. The first phase would screen for significant threat. The second phase would characterize the threat as coming from a chemical class or a particular chemical itself. The Third phase would use the results of Phase 2 to guide remediation efforts and test for success. Schematically, the concept is this:



Phase 1

INORGANIC

Spark –source mass spectrometry was chosen for this phase of elemental {primarily inorganic} determination. The technique was capable of detecting almost all the elements of the periodic table and certainly all the elements of concern. At low trace levels the precision was +/- 100% of actual and this was acceptable for this stage. Solid samples and deposited extracts dried to solid residue could be examined and the sample throughput rate was high

ORGANIC

Based primarily on experience in combustion programs, it was decided that the way to do the organic in Phase one was to extract the organic content of a sample with dichloromethane using Soxhlet extraction. The extract would be concentrated in a Kuderna-Danish evaporator and then solvent exchanged to cyclopentane. An aliquot was then placed on a silica column and the sample eluted using step gradients from hexane to methylene chloride to methanol. Fractions would be collected sealed and stored but an aliquot would be divided in two and the total 'chromatographable organics' over the range C5-C12 determined by gas chromatography in a method analogous to simulated distillation. The other part would be evaporated and the residue, if any, weighed. The result was a series of total organic content by weight in fractions varying from relatively non-polar to quite polar by chromatographic inference. Samples with a mass content above a predetermined limit would also have IR and low resolution mass spectrometric determinations done.

BIOLOGICAL

The particulate collected and fractionated dynamically by size in the sampling train was 'fed' to rabbit alveolar macrophage. The macrophage's normal function is to remove particles from the lung by ingestion and digestion. A sufficiently toxic particle will kill the single-cell phage. The Ames assay of 1975 consisted of treating the growth media of the bacteria with an aliquot of the sample or sample fraction and observing whether the colony survived. The strain used could no longer synthesize an essential nutrient and must get it from the medium. If the sample's contents caused mutation, the ability to synthesize cysteine returned. A variation using liver cell activation of the sample before the Ames test was also part of Phase 1

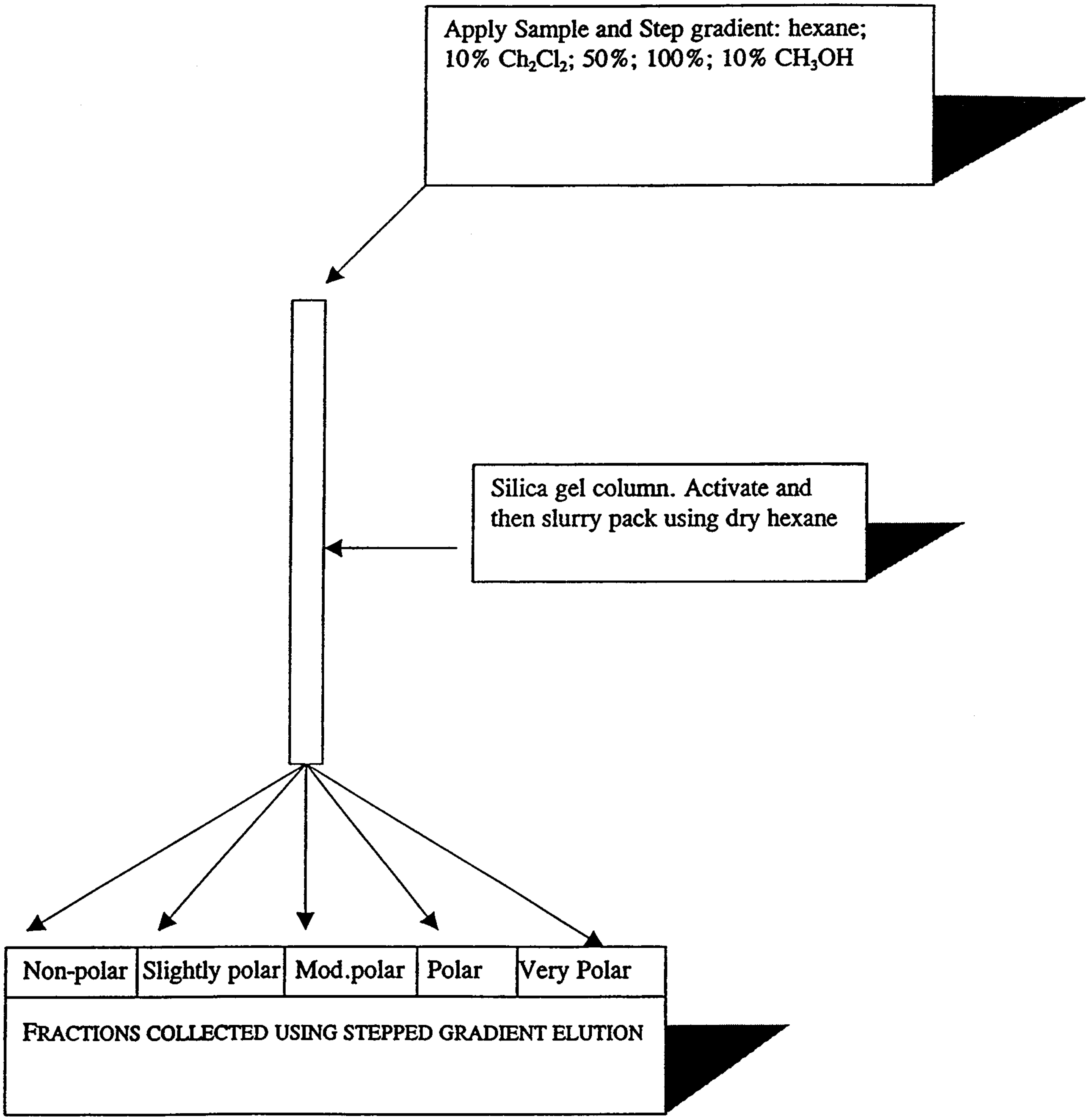


Figure 3. The fractionation scheme of Phase 1

Result of Phase 1

The combined findings of the particulate and extractable organic analyses coupled with the biological test responses permitted identification of areas of highest concern, directions for Phase II reexamination and even the likely "chemical class" of the offending components in the case of organics. Roughly, one in 10 were carried into the next phase for further chemical characterization.

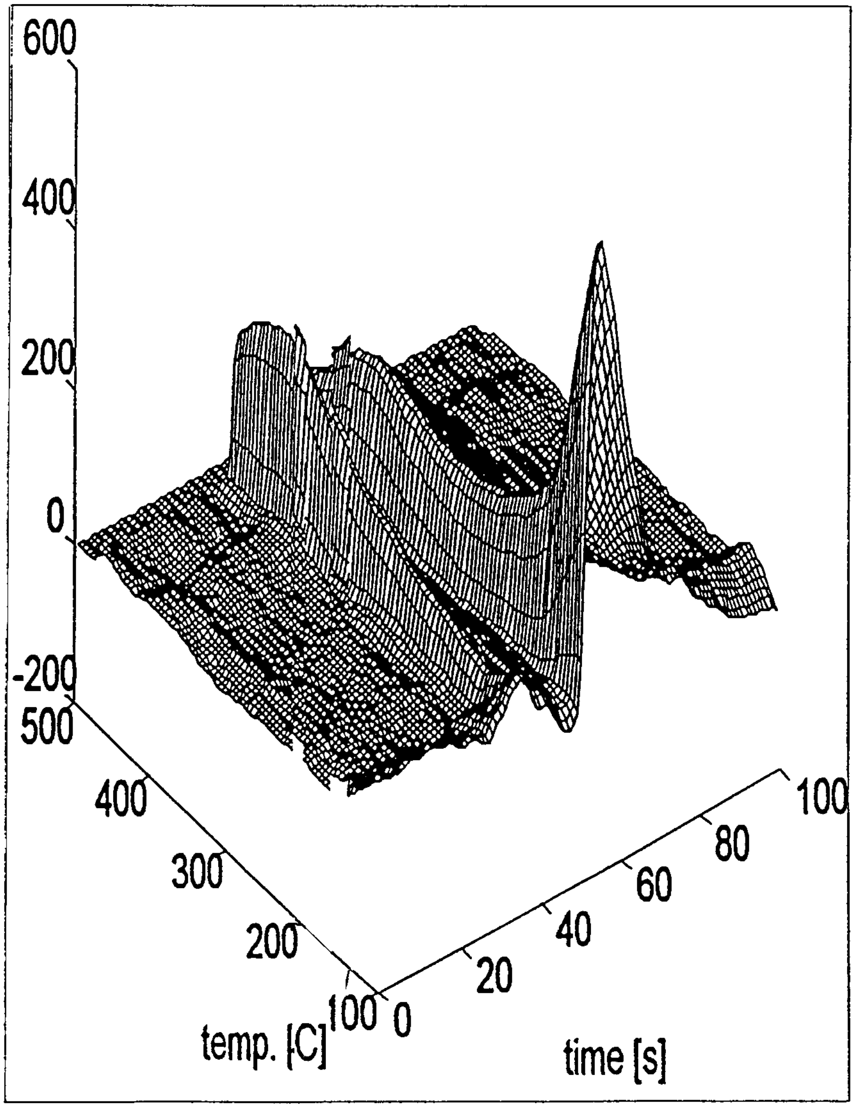
There is an anecdotal example that illustrates the success of this approach. It involves mobile source emission - specifically diesel exhaust. Samples were run through Phase 1 screening and the most surprising result was that the most mutagenic fraction was not the relatively non-polar, PAH-containing fraction(s) but a polar fraction in chromatographic terms. One can conceive of formation of 3-, 4-ring PAH's in the combustion of diesel fuel and that happening in the presence of N2, and O_2 at relatively high pressures could lead to nitro-PAH. However, the nitro-compounds are haptens not mutagens. Well, the Ames test as done in this case had both sample and liver-cell-activated sample results {One mixes sample with a suspension of liver cells apparently}, One liver component is a nitro-reductase and as such would convert NO_2-groups to NH_2. Aminopyrene is, for example a powerful carcinogen and hence a mutagen. Phase 2 studies confirm this chemically. The point is that the approach revealed not only the suspect carcinogens - the PAH's - but alerted the study members to the *in situ* synthesis of a powerful carcinogen's precursor in the exhaust.

Research in Basic Measurement Science - Analytical Chemistry

The example I have chosen to use is one that involves 10-year+ collaboration between my laboratory and those of the Institute of Chemistry of the Estonian Ministry of Education into the question of time-varying, sample streams. The goal is to find ways in which the output of the measurement effort is multi-dimensional in nature and in which the variables studied are largely orthogonal. These methods would then be subjected to the powerful techniques of 'chemometrics' in hopes of providing insights into complex samples and complex chemical phenomena. The example chosen is a method called 'Thermochromatography' or 'Thermo-gas chromatography" [ThGC]. Originally developed by Professor Kaljurand and Dr. Koel of the Institute, it has been applied to such varying samples and phenomena as pyrolysis and ignition of polymer and rubbers, to the thermolysis of oil shale and to evolving gas analysis of inorganic salts and mineral specimens including Martian soil simulants. It is an adaptation of headspace sampling an analysis in a sense. The combination of multidimensionality of response and chemometric data treatment reveals a great deal of useful chemical information. The method is clearly applicable to contaminated soils, incinerator waste and feed, etc.

The ThGC Method

The ThGC method involves the controlled heating of a sample using a gradient in temperature over time. The heating is carried out in an inert furnace that is a replacement for the inlet of a conventional gas chromatograph and through which inert carrier gas passes. The output of the pyrolysis cell passes through a sampling valve to waste. At programmed intervals and under computer control, samples are diverted into the open -tubular or 'capillary' column of the chromatograph where the components are resolved into a chromatogram. The result is an array of chromatograms with each chromatogram associated with sample temperature at the time of sampling. Clearly the 'surface formed can be quite complex if many components are present and resolved. The Figure below shows such a surface for a simpler mix of components evolved.



As can be seen the response axis is 'detector' response and in this case, thermoconductivity change. The detector could be a FID/EC/ NDIR/ . The axes are temperatures at the time of sampling for the sample chamber and retention time.

It has been shown that the resulting data structure - a matrix of detector response at a given temperature and retention time - is 'factor analyzable'. Conventional factor led to the discovery that two rubbers when blended react to form an non-separable third substance which has its' own pyrolysis behavior distinct from the pure rubbers themselves. It has been used to determine the effect of phosphate flame-retardants on pyrolysis behavior. Interestingly, it reveals that these additives actually lower the pyrolysis temperature leading to the early development of a 'char-layer' on the polymer surface. This layer then acts as a rate-determining barrier to diffusion of pyrolysis products to the surface and ignition is retarded. Along more environmental chemistry lines, we have shown that "evolving factor analysis' reveals the individual component chromatograms in a complex series of stages of thermolysis of oil shale. These were compared to the results of supercritical fluid extraction of shale and the behavior of the lower molecular weight, extractable fraction is much like that of the lower temperature evolving complex from heated shale. This is now being applied to a variety of shales of known heat content, etc. in hopes of deriving by simple means, information related to heat content at each temperature of an entire temperature range.

Acknowledgements

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