

NOVEL DIMENSIONS IN ON-LINE PROCESS SPECTROMETRY

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INTRODUCTION

The myriads of novel chemical processes the new millennium may be expected to bring to future generations will require increasingly sophisticated process characterization and monitoring techniques. Over the past decades the advantages of on-line, in-situ and/or real-time spectrometric techniques have been widely demonstrated. The main challenges for the new millennium will be: to achieve higher information yields and sample throughputs; to develop intelligent devices that interpret their own measurement data; to close the feedback process control loop; to probe harsh reaction environments in real-time; and to reduce total lifecycle costs for on-line spectrometry equipment.

INCREASING INFORMATION YIELD AND RATE

As discussed convincingly by Hirschfeld [1] and by Giddings [2], the most effective way to achieve higher information yields is to couple two or more compatible analytical techniques into a single "hyphenated" tandem method. Well documented examples include GC/MS, LC/MS, MS/MS, GC/IMS and GC/FTIR. (It may be noted that the term "hyphenated" - popularized by Hirschfeld - is somewhat of a misnomer since IUPAC nomenclature prescribes the use of forward slashes rather than hyphens to depict tandem instrument configurations). Hyper-hyphenated methods, featuring as many as four different analytical instruments in tandem have also been described, e.g. TG/GC/FTIR/MS [3]. Even more analytical dimensions can be added through "tandem-in-time" configurations such as in ion trapping MSⁿ methods, with n readily achieving values of 6 or 7 [4]. Also, it should be pointed out that as many as four useful analytical dimensions can be added by recording temporally [5] as well as spatially resolved spectra. An example of the use of time-resolved, on-line MS data to deconvolute a complex mixture of coal pyrolysis products, evolving from a small Curie-point pyrolysis reactor, into its main maceral constituent patterns, is shown in figure 1.

Unfortunately, our ability to add analytical dimensions has greatly outpaced our ability to process and interpret multidimensional data. Some progress is being reported in the development and application of principal component analysis techniques for three-way data matrices [6]. Also, the class of algorithms loosely described by the term ANN (artificial neural networks) is in principle capable of handling n-dimensional data outputs [7]. However, most of us are still struggling to comprehend multivariate data analysis results for two-way data matrices. Clearly, processing and interpretation of n-way data matrices is an area with much room for progress in the new millennium.

Whereas hyphenated methods are widely known for their ability to increase information yields, less well recognized is their potential for increasing analysis speed. At first sight it is counterintuitive that the coupling of two instruments in tandem could produce shorter analysis times. However, as pointed out by Giddings [2], to the extent that the information provided by independent, the resolving power of the tandem instrument equals the product of the resolving powers of the two modules. Since many analytical techniques can trade resolving power for speed the required minimum resolution for a given analytical application can often be reached with both modules operating in a high speed, low resolution mode, as illustrated in figure 2.

Interestingly, low resolution analytical modules also tend to be easier to miniaturize (or, perhaps more correctly stated, miniaturization tends to result in lower resolution) leading to the paradoxical conclusion that hyphenated methods may well lend themselves better to miniaturization and micro-miniaturization and, thus, to use as on-line analytical devices. The added complexity of the control electronics and software required to control hyphenated devices versus single stage modules may hardly increase the size and cost of large-scale-integrated electronic chips. In short, the future for hyphenated techniques in on-line process analytical applications is likely to be equally bright as in today's conventional analytical laboratory environment where the majority of new GC systems purchased is now equipped with an MS "detector".

PROBING HARSH REACTION ENVIRONMENTS

The suitability of stand-off spectroscopic techniques for probing high-temperature, high-pressure, high-radiation, highly corrosive and/or abrasive environments is widely known and is only limited

by the relatively low resolving power for complex chemical mixtures, by the availability of suitable window materials, and by the optical properties of the reactor contents. Since continuing progress can be anticipated in all these problem areas, the role and importance of stand-off spectroscopic process analysis techniques may be expected to help increasing over the next few decades.

Compared to stand-off techniques, the suitability of typical point detection methods (i.e. methods requiring physical transport of molecules, sampled at a given point in space and time, into the detector) for probing harsh reaction environments is less immediately obvious. Yet, the superior separation and identification capabilities of point detection methods such as MS (with or without chromatographic pre-separation) have time-and-again induced scientists and engineers to use MS-based methods in highly forbidding environments. An example of the use of on-line GC/MS for monitoring a 600 F flue gas stream, laden with abrasive ash particles, on the 7th floor of a rumbling, dusty coal combustor situated in a building subject to circadian temperature variations in excess of 50 F, is shown in figure 3.

Fortuitously, the use of rugged sample probes lined with fused silica, quartz or other refractory materials is often compatible with the required operating conditions for a given point detector, particularly in combination with highly flexible, readily heatable, capillary transfer lines. This approach enables successful coupling of GC/MS instruments to reactor environments with pressures in the several thousand psi range, including supercritical environments (see figure 4) and temperatures in excess of 1800 F [8]. Nonetheless, there is considerable room for further improvement in sample transport systems, e.g. capable of entraining fine particulate matter indigenous to the sample stream or produced with the help of ablative laser probes. Another, as yet unexplored, sampling strategy would be to enlist the support of "stand-off sampling techniques" for point detectors, e.g. by shooting fast traveling vortices, capable of entraining vapors as well as fine particulate matter, across reactors into the point detector inlet.

REDUCING INSTRUMENT LIFECYCLE COST

Most on-line spectroscopic techniques have a reputation for high capital equipment cost, very high maintenance cost and exorbitantly high operating cost (due to the need for highly trained operators). As a result most production managers are understandably reluctant to introduce novel spectroscopic techniques into existing process operations unless there are serious problems. Consequently, new opportunities for on-line spectroscopic techniques must primarily may need to be sought in the development and testing of novel processes and pilot plants.

Recent breakthroughs in the design of highly miniaturized and/or microfabricated MS analyzers promise to drastically change the instrument lifecycle cost equation for this type of analyzer within the next few years. Not only are these miniaturized MS analyzer modules (including ion source and detector) likely to become available commercially at a cost of less than US \$1,000 but — due to the difficulty of exchanging or cleaning the very small ion source or detector components — they are also meant to be disposable in case of failure or deterioration. The big advantage of this approach is its potential to greatly reduce overall maintenance cost.

Presently, no fewer than three such disposable MS devices are either already available (viz. Ferran's miniature quadrupole head [9]), or may become available soon (viz. a subminiature double focusing magnetic device and an FTICR type MS device; both expected to be introduced at the January 2000 ASMS conference in Sanibel). Present limitations include limited resolving power (i.e. the product of mass range and resolution), as well as relatively low sensitivity and/or speed. As discussed earlier, hyphenation (e.g. by adding a micro-GC preparation module) may eventually help overcome some of these limitations. A related area where major improvements will be needed to match these new developments in MS analyzer technologies is high vacuum pumping. Current high vacuum pump technology is expensive and difficult to miniaturize further.

Finally, the major cost of using on-line spectroscopic techniques, viz. the need for highly trained operators, is only going to come down when the above-mentioned multidimensional data processing and interpretation steps can be fully automated and integrated into the design of the spectroscopic instrument. In other words, development of sufficiently "smart" spectroscopic devices is likely to be the final hurdle on the way to broad acceptance of on-line spectroscopic technologies into the full scale process analysis marketplace.

CONCLUSION

Rapid development of MS-based and other miniaturized and micro-miniaturized, MS based on-line spectroscopic methods can be expected over the next few decades, eventually resulting in the presence of multiple, networked, disposable, hyphenated devices per reactor. The temporally and

spatially resolved information produced and processed by the network will allow an unprecedented degree of process control and quality assurance, as well as rapid troubleshooting capability if and when human intervention becomes necessary.

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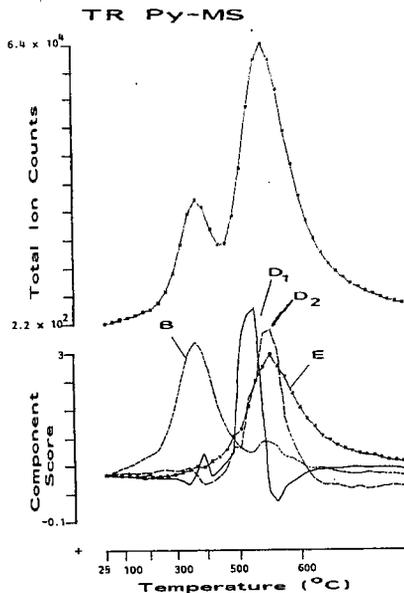


Figure 1. Example of the use of time-resolved mass spectral profiles to produce an additional analytical dimension. The total ion profile in (a), representing Curie-point pyrolysis products evolving from a coal sample, is being deconvoluted into four maceral-like components (b) by means of multivariate statistical analysis methods. For detailed information see reference 5.

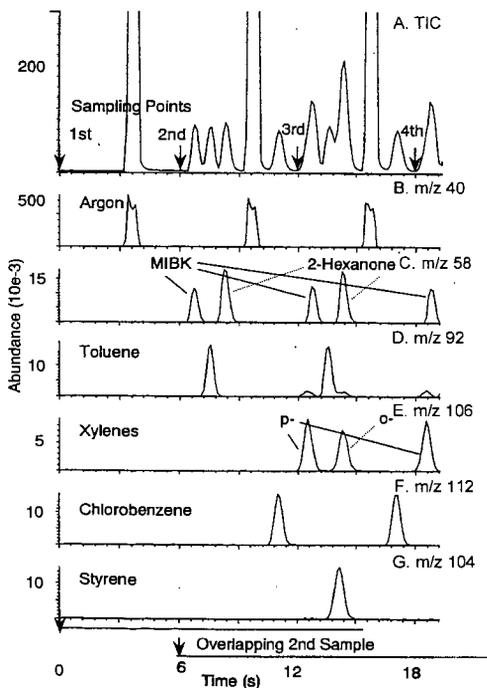


Figure 2. Example of fast, repetitive hyphenated (GC/MS) analysis demonstrating complete resolution of 9 components in 2-dimensional (GC/MS) space although the individual component techniques resolve only 5 (GC) and 7 components (MS), respectively. For detailed information see reference 10.

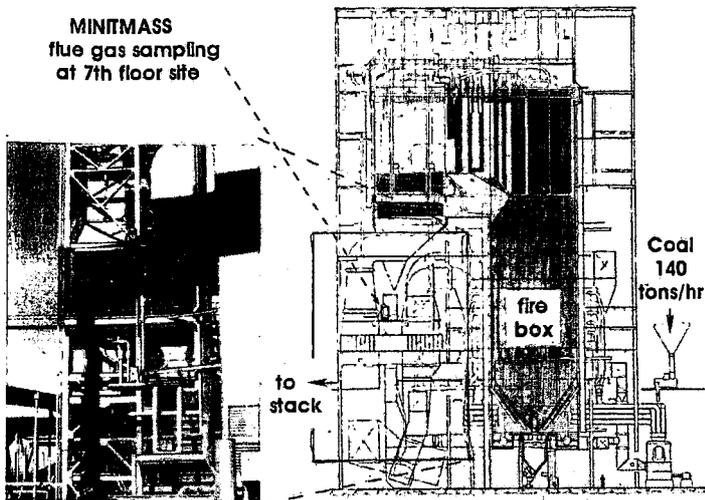


Figure 3. Example of operating a GC/MS instrument, nicknamed "minitmass," in a harsh industrial environment.

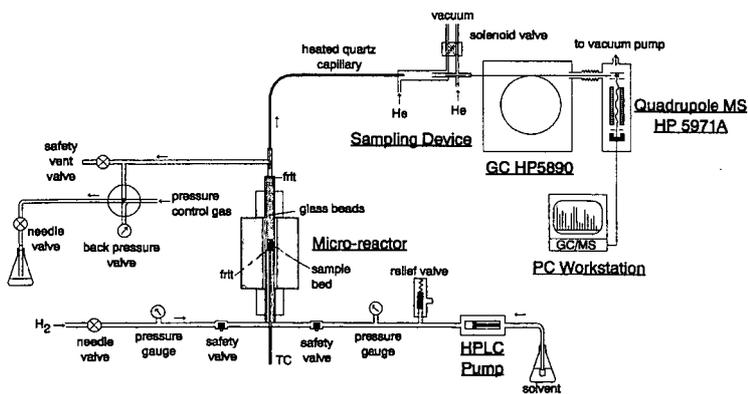


Figure 4. Example of an on-line GC/MS experiment coupled to a bench-scale high pressure reactor operating under supercritical conditions. For detailed information, see reference 8.