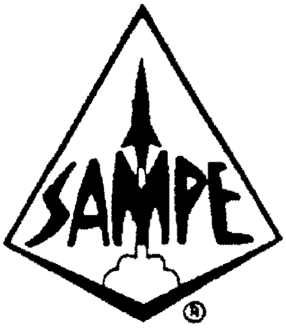
SOCIETY FOR THE ADVANCEMENT OF MATERIAL AND PROCESS ENGINEERING



ENVIRONMENT IN THE 1990's
A GLOBAL CONCERN

ENVIRONMENTAL MONITORING USING CHEMOMETRIC TECHNIQUES WITH THE COMING GENERATION OF SMART ANALYZERS

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ABSTRACT

Chemometrics is the application of advanced statistical and mathematical techniques to the field of analytical chemistry. Inexpensive but powerful microcomputers will become a standard part of the coming generation of analytical instruments. This technology makes it possible to incorporate sophisticated pattern recognition algorithms into these instruments, liberating them from the laboratory and turning them into "smart analyzers" that are capable of a variety of real time chemical identification, quantification, control and alarm tasks. Examples presented include on-line UV-VIS-NIR absorption spectrometers for analysis of organics, in-situ Atomic Emission analyzers for metals, and Surface Acoustic Wave (SAW) detectors for gas analysis.

These developments have important implications for the field of environmental monitoring. Smart analyzers will make it possible for environmental monitoring to be performed inexpensively, at more frequent intervals without the need for direct participation by scientific personnel, and with results available instantaneously. These developments can permit a closer degree of monitoring by potential sources of pollution and by enforcement agencies.

KEYWORDS: Analysis - Chemical, Testing/Evaluation/Characterization, Chemometrics, Spectroscopy.

1. FEATURES OF SMART ANALYZERS FOR ANALYTICAL CHEMISTRY

Anyone reading the title of this paper who has visited an analytical laboratory recently must wonder just how much "smarter" instrumentation can become. After all, instruments that are capable of quantitative analysis at part per billion or part per trillion detection limits seem to be smart enough for most environmental uses. If you are on the receiving end of environmental enforcement actions, you may feel that today's instruments are already too "smart" for their own good. But intelligence in instruments, like intelligence in people, is measured as much by diversity as by depth. Laboratory instruments are the idiot savants of analytical chemistry: they can perform a single function exceptionally well, but have few other capabilities. There are several capabilities that can be used as signs of intelligence for analytical chemistry instruments.

1.1 Information Processing. Smart analyzers have a wide range of capabilities which result from a highly developed ability to capture and process information. This capability is a function of integral sensors that permit information to be detected and the presence of built-in computational power to extract and process information. The computational power includes memory for stored data bases or other reference sets, as well as algorithms for use in extracting details from the detected information to compare with the stored information. The smarter instruments will be able to perform both qualitative and quantitative analysis with this information, and the smartest will be able to perform analysis of multiple chemical components.

1.2 Unattended operation. The less help required by the instrument, the smarter it is. Some instruments require prompting or set-up at various stages of the analysis. Some may require manual adjustment for each new analyte detected. Smart analyzers reduce or eliminate the need for these functions.

1.3 No reagents. These systems do not require the use of reagents, extractions, dilutions, or other procedures normally thought of as necessary for analytical chemistry. Specialists trained to execute procedural steps will not be needed. This will result in a fundamental change in the way chemical analyzers are applied, which will be as an element in a control system, not as an function to be performed outside of the control system.

1.4 Communications capability. Smart analyzers can not only produce analytical results, they can convert these results into information for display, storage, or transmission to external devices. Some smart instruments may even contain the ability to convert analytical results directly into operational instructions for actuators that are connected to or are part of the instrument.

2. FORCES INFLUENCING SMART ANALYZER DEVELOPMENT

2.1 Demand for decentralized analysis. The capabilities of analytical instruments often fall short of the actual needs that exist for close control of continuous processes through the timely availability of analytical results. The analysis of samples at remote times and locations does not provide the information needed for control of continuous processes, but remote analysis may be necessary due to the need to use high cost specialized equipment operated by skilled personnel in a controlled environment in order to obtain the necessary analytical results. Untimely results may be better than no results at all, but this does not eliminate the original need for control information. If the factors that limit timely analysis at the point of use (cost, specialization, operator skill, environment) can be addressed with new technology, the technology will be in demand. The current state of instrumentation in the chemical and biological field has been compared to the state of computer technology twenty years ago, where large centralized machines were presided over by specialists who stood between the user and the technology. Eventually, technological changes improved performance and reduced costs, making it possible to empower users by decentralizing the technology.[1]

2.2 Affordable computational capability. As the cost and size of computational hardware declines, it becomes affordable to incorporate this capability directly into analytical instruments. Computer-based instruments are one key to achieving the performance capabilities required for decentralized operation of chemical analysis functions, including the information processing, unattended operation, reagentless and communications capabilities previously discussed.

2.3 Improvements in sensor technology. The other key to decentralized operation is in sensor technology. The capability to detect some measurable quality in the matrix being analyzed, convey the information to the point of analysis, and convert it into data that can be acted upon by the analysis routines in the instrument is essential. The quality detected in the matrix may be a natural condition or a variable response to some form of stimulation generated by the analyzer or in the sensor itself. Spectroscopy, for example, detects responses to stimulation over a portion of the electromagnetic spectrum. This stimulation is generated by a light source located within the instrument. Currently, chemical sensors are evolving in two directions. Some sensors are highly specific to a particular chemical or class of chemicals. Sensors at the other end of the scale are more appropriately classified as response detectors since they are limited by the type of stimulation applied, not by the specific chemicals exposed to the stimulation.

2.4 Development of analysis software. Computational power and sensors mean little without algorithms capable of converting detected information into analytical results. The less specific a sensor is to a particular chemical, the more capability is required from the analytical models in order to convert the detected information into qualitative and quantitative results, as shown in Figure 1. If a sensor is proportionately responsive to one and only one chemical substance, the burden for qualitative analysis is eliminated and the issue of quantitative analysis is simplified. The greater the range of analyte responses from the sensor, the more burden is placed upon algorithms to extract and interpret information from a multi-component chemical matrix to be analyzed. As complexity increases, so does the need for computational capability. The only way computational capability can be conserved is through the efficient use of it by the software. The development and application of statistical and mathematical techniques for analysis, collectively known as CHEMOMETRICS, has been an important factor in the emergence of smart analyzers.

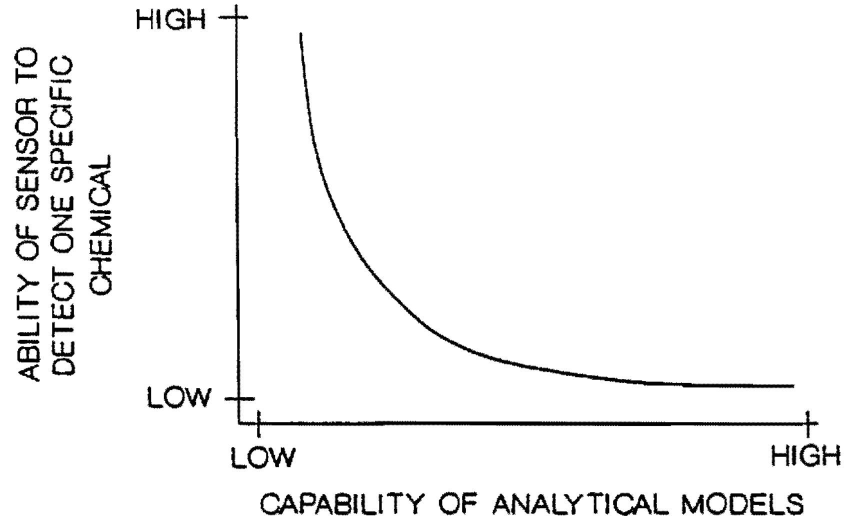

Figure 1. Sensor ability vs. model capability

2.5 Available control system elements. A final factor influencing the emergence of smart analyzers is the availability of standardized technologies for use in control systems. A vast selection of communication interface accessories, actuators and programmable controllers are available. Too often, the weak link in the design of a control system for chemical or environmental use is the limited capability of the chemical sensors. As demand for smarter control systems increases, so does demand for smarter instruments to be used in these systems.

3. ENVIRONMENTAL ANALYSIS NEEDS

Environmental analysis can be thought of as a process control application. In fact, the equipment and processes used in pollution control are very similar to those used in other chemical processing applications. The objective is to produce a product that conforms to specifications, although in this case the products must be within the specified tolerances that make them good enough to legally throw away. Environmental analysis requirements are often a function of the purpose served by the analytical results. These requirements also influence the degree of smartness required of analytical instruments. An example is the analysis of groundwater for the presence of contaminants which require three different types of analysis.

3.1 Screening. The requirement is for rapid, low cost test methods that can be used directly at a site to determine whether or not specific contaminants are present at or above a certain threshold limit.[2] Screening is used to quickly establish whether more comprehensive analysis is needed. If the objective is to verify that a gasoline storage tank has not leaked, the analysis requirement is limited to indicators of contamination from gasoline. If the range of interest at a site is more diverse, such as verification that a sanitary landfill liner has not leaked, then the capabilities of the analyzer must be much higher (or several analyzers must be used). In either case, it is still preferable to perform a rapid analysis in the field, than to extract and transport samples for remote analysis at a laboratory. The fastest way to evaluate a site is to "transport the laboratory to the sample".[3] The smarter the instrument, the easier this is to do.

3.2 Characterization. This requirement is for analysis of many different chemical parameters, all with very high degrees of quality assurance for law enforcement and remediation design purposes. This is a task that is mandated to be performed in accordance with specified laboratory procedures that are manually supervised. This is probably for the best, since smart instruments can do many things, but they can't testify in court. Unfortunately, when these characterization procedures are used for screening or monitoring purposes, enormous costs are being imposed that could be avoided with the use of smart analyzers.

3.3 Monitoring. Monitoring is the periodic analysis at a site for contaminants that have previously been identified. The same contaminants are always the object of the analysis. The analysis is usually performed for one of two purposes: to assure the continued absence of contaminants (i.e. to verify the integrity of containment systems) or to document trends (i.e. to measure reductions in contaminant concentrations during remediation). Smart analyzers can reduce costs, especially labor costs, and can provide immediate analytical information for health protection or process control purposes.[4] Although the purpose of monitoring is straightforward, the performance may be a challenge. Groundwater is actually a complex multicomponent chemical matrix consisting of many different substances that reflect the adjacent geology such as calcium, magnesium, iron, manganese, sodium, potassium, bicarbonates, sulfates, chlorides, nitrates, and silica.[5] Unnatural contaminants being monitored must be identified within this complex matrix, given all possible intercomponent reactions and interferences. A measure of intelligence for the analysis system is the capability of "extracting information from measurements corrupted by noise".[6] This task is performed by chemometric analysis techniques.

4. CHEMOMETRIC ANALYSIS TECHNIQUES

Analytes must often be recognized and measured in media that contain numerous components. An example is the use of absorption spectroscopy for analysis of chemicals in water. The absorption spectrum detected across a range of wavelengths will be a function of the combined spectra for all absorbing components in the water. A smart instrument for absorption spectroscopy must be able to nor only detect the spectrum, but also must be able to recognize and measure individual constituents based on their contribution to the detected absorption spectrum. There are three basic steps involved in the chemometric analysis of absorption spectra, as shown in Figure 2.

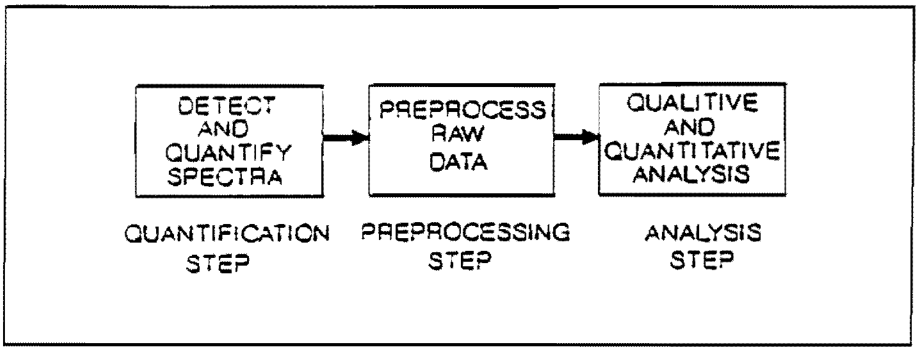

Figure 2. Chemometric analysis steps

4.1 Quantification. This step involves converting detected spectra for the matrix under analysis and previously processed calibration (learning) sets into numerical values that can be processed using mathematical and statistical procedures. Quantification for absorption spectroscopy is governed by Beer's Law, which relates the amount of light absorbed to the absorptivity of the media, the path length of the light and the concentration of absorbing components in the solution.[7] For a matrix where all of the absorbing components are known, total absorption will be a function of the sums of all absorbing components based upon their individual concentrations. Equations can be defined for several wavelengths and simultaneously solved. Knowledge of all absorbing components is unusual, so an inverse technique that defines concentration as a function of absorbance has been developed.

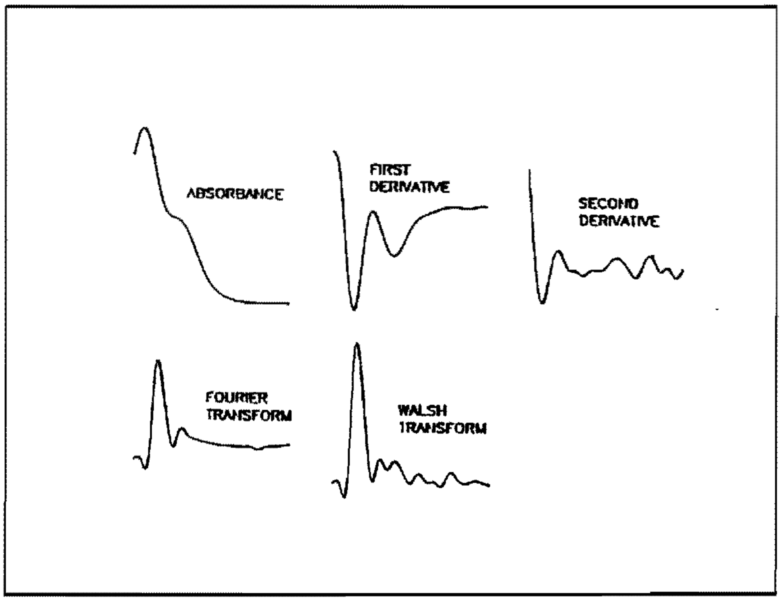

Figure 3. Transformations

4.2 Preprocessing. Preprocessing of spectra is often performed to aid in the analysis of multi-component solutions or to adjust for noise or drift. Typical techniques include the use of first or second derivatives of the absorption spectrum and the use of Fourier or Walsh transformations.[8] Figure 3 illustrates how absorption spectra can be transformed using these techniques. If two original spectra were very similar but not identical, examination of their transformed spectra might reveal their differences. Conversely, if the differences were due to the presence of noise of drift, comparison of transformed spectra may reveal the similarities not evident in the raw data.

4.2.1 Principal Components Analysis. Principal Components Analysis (also known as Eigenvector analysis, Hotelling transformation, or Karhunen-Loeve transformation) use statistically determined quantities to rotate the coordinate system such that the original information that may have been aligned on several axes becomes aligned on only a few axes. In effect, the variables that are highly correlated with one another can be treated as a single variable, thus simplifying the analysis.[9]

4.3 Analysis. If information from a calibration (learning) set or data base of stored information is available, parametric techniques can be used to compare information from the unknown solution with information from the known solutions. Two techniques are frequently used.

4.3.1 Regression. Stepwise linear regressions are used to characterize multiple analytes using information at multiple wavelengths.

4.3.2 Discriminant Analysis. Discriminant analysis is a clustering process which defines linear decision boundaries between information clusters for known concentrations of analytes, and assigns unknowns to an appropriate cluster based upon detection of significant characteristics for the unknown.[10] Figure 4 is a graphic representation of this process.

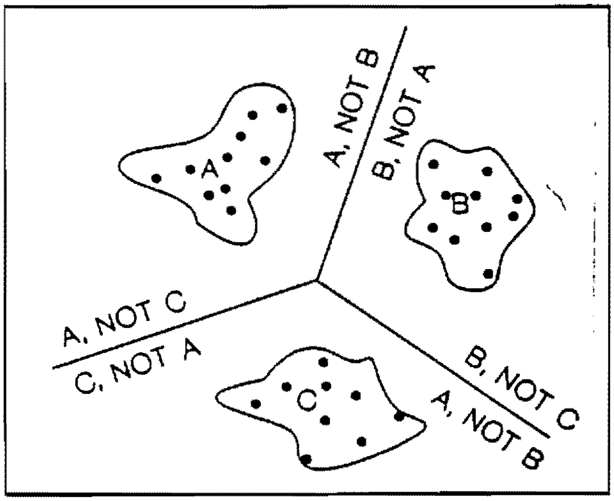

Figure 4. Discriminant boundaries

4.4 Emerging techniques. Emerging techniques for analysis include experimental methods such as inductive learning and neural networks, especially for problems that cannot be simplified through principal components analysis. A technique that shows great promise is the Lattice-K Nearest Neighbor technique, where known values for variables are organized into the nodes of a lattice. Predicted values for an unknown are based upon relative distances of variables for the unknown with those of the nearest neighbors in the lattice.

5. APPLICATION REQUIREMENTS FOR SMART ANALYZERS

Smart analyzers can best be used in applications that have special requirements that are satisfied by the unique capabilities of these instruments.

5.1 Decentralized location. Although smart analyzers can be of use in a laboratory environment, their basic purpose is to place analytical capabilities at non-laboratory locations, preferably at the point where the analytical information can be used to make control decisions. There are three possible relationships between the instrument system and the matrix being analyzed.

5.1.1 On-site analysis. The instrument is located in close proximity to the matrix to be analyzed, but is not connected to it. An operator must initiate the analysis by providing a sample. Analytical results may or may not be automatically converted into control decisions, but most likely this step will also require operator intervention.

5.1.2 On-line analysis. The instrument is located close to the matrix to be analyzed and samples are automatically extracted and conveyed to the analyzer or to a sensor that is connected to the analyzer. This arrangement is usually the result of the need for analytical results at frequent intervals, so it is likely that these results will need to be automatically communicated for control or alarm purposes.

5.1.3 In-situ analysis. The sensor is located within the matrix to be analyzed and is directly connected to the instrument. Results from this arrangement are usually needed continuously and are used for control or alarm purposes. This arrangement also has application where the samples have dangerous qualities (radioactive, highly toxic, etc.) which impose restrictions on handling.

5.2 Reduced operator skills. Smart analyzers can put chemical analysis capabilities at the disposal of users who require analytical results but are not skilled in chemical analysis procedures. Smart analyzers can also result in improved analytical results over laboratory methods, even though such methods are frequently assumed to be superior. Laboratory methods require careful sampling and sample handling. Failure to properly handle samples is a major source of analytical error, but elimination of the need to extract and process samples can eliminate this source of error. In the case of highly volatile or fragile samples, direct analysis by smart instruments may produce superior results.

5.3 High sample frequency. In applications where many samples must be processed, smart analyzers can result in cost, operational and control advantages. On-line or in-situ analysis can provide analysis continuously or at specified intervals.

5.4 Immediate use of outputs. Smart analyzers may have their greatest application where there is no margin for long time intervals before analytical results are available. Safety monitoring or control of continuous processes demand immediate and continuous flows of information.

6. EXAMPLES OF ENVIRONMENTAL APPLICATIONS

A number of smart analyzers are presently available or are under development for use in environmental applications.

6.1 UVAS. Ultraviolet-visible array spectroscopy (UVAS) is an existing laboratory technique that has incorporated newly developed technology to perform real time analysis of heavy metals, unsaturated organics and aromatics in water.[11,12] A broad spectrum of light is generated by a Xenon lamp in the analyzer, and delivered to the water using fiber optic cables. The light is transmitted through the water in specially designed optical probes suitable for on-line of in-situ analysis. The light remaining after transmission through the water is collected and returned to the analyzer through a companion fiber optic cable, where it is dispersed into wavelengths by a grating and projected onto a 1024 element photodiode detector array. The detected absorption signature is processed using chemometrics techniques. Existing applications include identification and measurement of iron and nitrates in nutrient solutions, detection of multiple contaminants (metals, nitrates, organics, aromatics) in groundwater, detection of regulated materials (chromium, zinc, mercury) in industrial wastewaters, and water treatment quality parameters (copper, iron, molybdate, triazole, phosphonate) in industrial process and cooling waters.

6.2 LAES. Liquid Atomic Emission Spectrometry (LAES) uses a photodiode detector array, similar to that used in UVAS, but with a high energy arc discharge directly in the liquid as the source of excitation. This generates an atomic light emission which is conveyed from the water to the analyzer through fiber optic cables for analysis using special pattern recognition techniques. Qualitative analysis is performed by the detection of emission lines, while quantitative analysis is a function of intensity. LAES had recently been demonstrated for analysis of metals, hydrogen, and sulphur in conjunction with a recent NASA contract.[13]

6.3 NIR. On-line real time Near Infrared (NIR) analysis of liquids (using transmissive techniques) or solids (using reflective techniques) is a technology that is growing in acceptance. It is arguably the most well developed application of chemometric analysis techniques, especially in the food processing industry.

6.4 SAW. Surface Acoustic Wave (SAW) array analyzers are under development for a number of environmental gas monitoring applications. SAW sensors use a dual oscillator arrangement where one SAW is coated with a sorbent material that is specific to a particular gas, while a second SAW remains uncoated. The frequency of the coated oscillator is compared to frequency of the uncoated oscillator, and is an indicator of gas concentration. Historically, the problem with such devices resulted from interferences from other gas species, resulting in a lack of specificity for the sensor. This problem can be overcome with array configurations consisting of several sets of oscillators with coatings that absorb different gas species at

different levels of solubility. This establishes a fingerprint that is specific for each gas and can be recognized using chemometric analysis techniques. Carbon dioxide and methane are two environmentally significant gasses that can be analyzed using this method.

7. CONCLUSION

Smart analyzers are an emerging technology that meet the needs of many chemical process control and monitoring applications, including environmental applications where real time analysis of multi-component solutions is highly desirable.

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