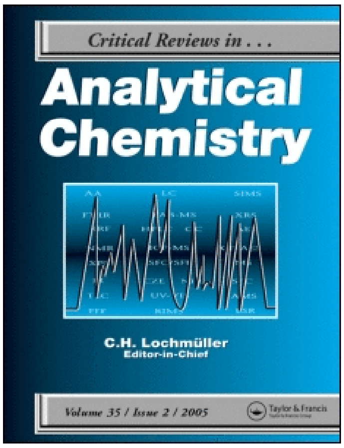

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ENVIRONMENTAL CHEMICAL SENSORS - NEW CHALLENGE AND OPPORTUNITY

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NEED FOR ENVIRONMENTAL CHEMICAL INTELLIGENCE

Environmental problems range from those that make life unpleasant or difficult to those that could lead to a major alteration of the present ecosystem and our ability to survive. Most of the well publicized environmental issues such as the effect of fluorocarbons on the ozone layer in the upper atmosphere, the effect of phosphates on natural water, adverse health effect of pesticides, etc., fall nearer the "make life difficult" end of the spectrum [1]. A good example for an environmental sensor in a "make life difficult" category is the monitoring of stack emissions from industrial processes. While large chemical and power plants can afford fairly expensive equipment for monitoring and treatment of emissions, smaller plants will have to rely on less expensive alternatives. It has also recently been found that in many urban areas the major contributors to air pollution are non point sources such as dry cleaners and bakeries. Small businesses such as these cannot support expensive equipment for monitoring emissions, yet it is clear that if progress is to be made in improving air quality, these small sources must be monitored.

More serious environmental issues arise from the prolonged and concentrated production of military materials, namely transuranium materials for nuclear weapons. The waste generated in this process has created an environmental and health legacy of uncertain dimensions. Today, we face growing public concerns over exposure to past radioisotope releases, storage of nuclear waste, and the potential diversion of military nuclear materials for terrorist use. There may be few greater scientific responsibilities faced today than dealing responsibly and rationally with these substances.

The environmental cleanup of military nuclear waste is a major ecological problem common to all nuclear superpowers [2]. The Hanford Site, located in southeastern Washington State U.S.A.) , is a microcosm of the environmental and nuclear material management issues facing the U.S. Department of Energy (DOE). Hanford contains about one-third of all the radioactivity (446 million Ci), two-thirds of all high-level waste (244,000 m3), and almost one-third of all DOE waste sites (1400). (Table I). Because of their chemical and physical properties many contaminants will have a lasting ecological impact on historical scale (Fig. 1). For this reason there is no such thing as a geographicallu confined environmental problem. In other words the legacy of the Cold War is a truly international problem.

Contamination spreading that is monitored shows that each contaminant has its own dynamic behavior in the ecosphere. Tritium, alkali metals, and alkali earth cations travel through the environment quickly by convective transport. Spreading of heavy elements and actinides are slower, and their transport mechanisms are not well understood. Because the water table (upper boundary of the underlying aquifer) lies 60 to 100 m below the land surface at most Hanford disposal sites, many of the heavier elements appear to be held high in the soil column by filtration and ion exchange mechanisms.

Although the geography is different there are many common aspects of the Hanford site and the nuclear production facilities in the Former Soviet Union. A total of 120 metric tons of weapon-quality plutonium is estimated to have been produced within the former Soviet Union. A maximum of 30,000 m3 of high-level waste containing 823 million Ci is stored in stainless steel tanks. However, there have been significant releases of radioactive waste in the south Ural region and in Siberia. Most contamination took place in the 1940s and 1950s when reprocessing waste was discharged directly into adjacent rivers and lakes. Discharging nuclear waste directly to the ground continues at several Russian sites. For comparison, the Chernobyl (1986) accident, which directly affected the Baltic region, released 50 million Ci. The Three Mile Island (1979) reactor accident in the US released about 50 Ci.

The Baltic Sea has been used as a convenient dumping space for obsolete chemical weapons and industrial effluents since the end of the World War II. However, the biggest danger to the 80 million people population of the littoral countries of the Baltic region is apparently the nuclear waste contained only by an earthen dam in Sillamae, Estonia [3].

SCOPE OF ENVIRONMENTAL SENSING

The driving force behind environmental science is the need to obtain a rational and quantitative assessment of the ecological impact of past and present human activities on the future prospects for our continued existence. The development of a dynamic ecological model is the subject of this emerging scientific discipline. Because many of the interactions between man and environment are chemical in nature, chemical sensors are expected to play an important role in environmental science. Predictably, they have been called "environmental sensors" very much like "biosensors" became a poorly defined but popular catchword for a group of sensors that had anything to do with "bio-" several years ago.

Chemical sensors provide data about the chemical state of our surroundings, such as the atmosphere of our habitats, about the course of dynamic chemical processes taking place in chemical manufacturing plants, etc. However, in most complex sensing situations, the simple functional relationship between the concentration of some species in the system and the raw electrical output from the sensor for that species is rarely adequate. Interferences from other species present in the system often result in biased measurements. The response of analytical chemists has been to collect more data on the system under observation and attempt to de convolute the measurements.

Modern statistical techniques popularly known as chemometrics have been developed to overcome this measurement deconvolution problem. It has been amply demonstrated [4] that multivariate measurements, combined with modern data and system modeling methods, can produce information well beyond the limits achievable with individual sensors. Thus, the advanced data processing techniques have become an integral part of the sensing process.

Chemical sensors are only one component of characterization, which is defined as follows:

Characterization is the act of developing a model or understanding of the chemical, physical, and spatial properties of a system.

In this context, characterization can be seen as chemical intelligence, which provides operational information about the chemical state of the system under consideration. From the analytical point of view data is obtained from: (1) off-line, discontinuous, batch chemical analysis; (2) on-line, continuous, in situ chemical sensors and ex situ sensor systems; and (3) transformed into information through application of chemometrics. The chemical intelligence is an integral part of any environmental remediation scheme [5] and the chemical sensors used for continuous monitoring are only one part of it (Fig. 2) .

HIGHER ORDER CHEMICAL SENSORS

Analytical instruments can be classified according to the dimensionality of the data they produce. The dimensionality of the data defines the order of the system. For instance, a pH electrode, which takes one datum per measurement, is a zero-order instrument since a single point has dimension zero. A spectroscopic instrument, which measures absorbency as a function of wavelength, is a first-order instrument. Each measurement produces a vector of data. A vector, of course, is one-dimensional (a first-order tensor). There is a growing trend towards instruments that produce a matrix (second-order tensor) of data with each measurement. Typical examples are the "hyphenated" techniques, such as gas chromatography - mass spectrometry (GC-MS), and other types of time resolved spectroscopy. In these techniques, measurements are made as a function of two variables to produce a matrix of measurements. For example, in GC-MS the quantity of ions produced is measured as a function of their atomic mass and the retention time on the GC.

Single chemical sensors generally do not perform well in situations where many different chemical species are present, which is typically the case in environmental monitoring applications. This is the issue of chemical selectivity. Univariate sensors cannot reach the selectivity of modern analytical instruments in which the analytical separation step precedes the actual quantification step. However, the sensor approach offers the speed of information acquisition, portability, remote operation, and economy. It can be shown that higher performance can be expected from higher order sensors and sensor arrays. For example, it is impossible to detect the presence of an interferent with a zero-order instrument. There is no data with which to cross reference the measurement. In a first-order instrument, it is generally possible to detect the presence of interferents; however, it is not generally possible to correct for the interferents and quantitate the species of interest correctly in their presence. With a second-order instrument, both detection of interferents and quantitation in their presence is possible. It has been shown that the ability to deal effectively with unknown interferents is critical in applications of environmental sensors [6]. In the last decade individual zero-order sensors have been grouped to form first-order arrays whose output has been processed through advanced statistical and mathematical algorithms collectively known as chemometrics.

MINIATURIZATION

The requirement of multiple sensing elements leads to a different fabrication approach than has been used for zero order chemical sensors. Almost every type of chemical sensor can be made by using silicon-based microfabrication technology. In the context of the needs for environmental sensing the fabrication of multisensor arrays is particularly important. The requirements on lateral resolution of the fabrication process rarely exceed 5 μm; however, ability to deposit and geometrically pattern unusual combinations of materials is important. Because, during the course of its lifetime, the solid state device comes in an intimate contact with quite harsh environments new encapsulation procedures had to be developed. The microfabrication of environmental sensors is driven by the need for multisensor capability rather than by the size of the available sampling space.

The characterization of the nuclear waste clean-up often requires special handling procedures due to the extremely dangerous nature of the samples. Miniaturization of the radiochemical procedures by, for example, automated flow injection techniques provides an answer to that problem [7].

CONCLUSIONS

It is clear that there are many applications in environmental monitoring and remediation where no suitable sensor or sensor system exists and new devices need to be developed. It is expected that higher order sensors and automated flow injection and microseparation techniques will become the norm for environmental applications. This will require continued development of both sensing arrays, producing data of higher quality, and calibration and diagnostic methods, that turn this data into information.

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TABLE 1

PRODUCTION OF MILITARY PLUTONIUM AND RESIDUAL WASTE/RADIOACTIVITY BY COUNTRY

COUNTRY	Pu-239 Produced [tons]	Volume of High Level Waste [M^3]	Radioactivity [Mci]
USA	108.3	400,000	1,045
USSR	122.5	300,000	945?
UK	5.0	1,430	811
FRANCE	6.0	1,400	274

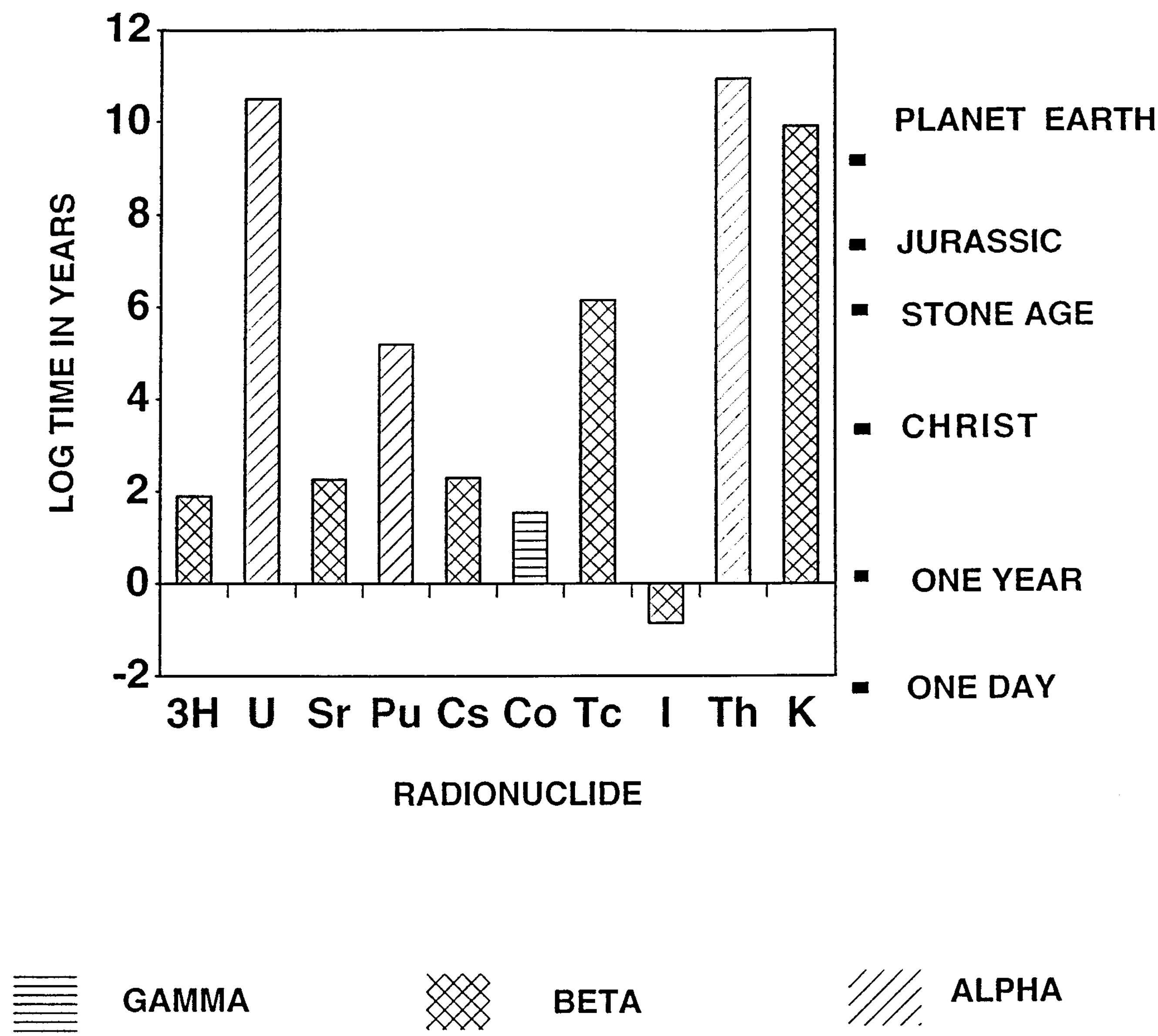

Fig 1 The time required for decay of principal radioisotopes to 1% of their original amount measured on human and geological time scale

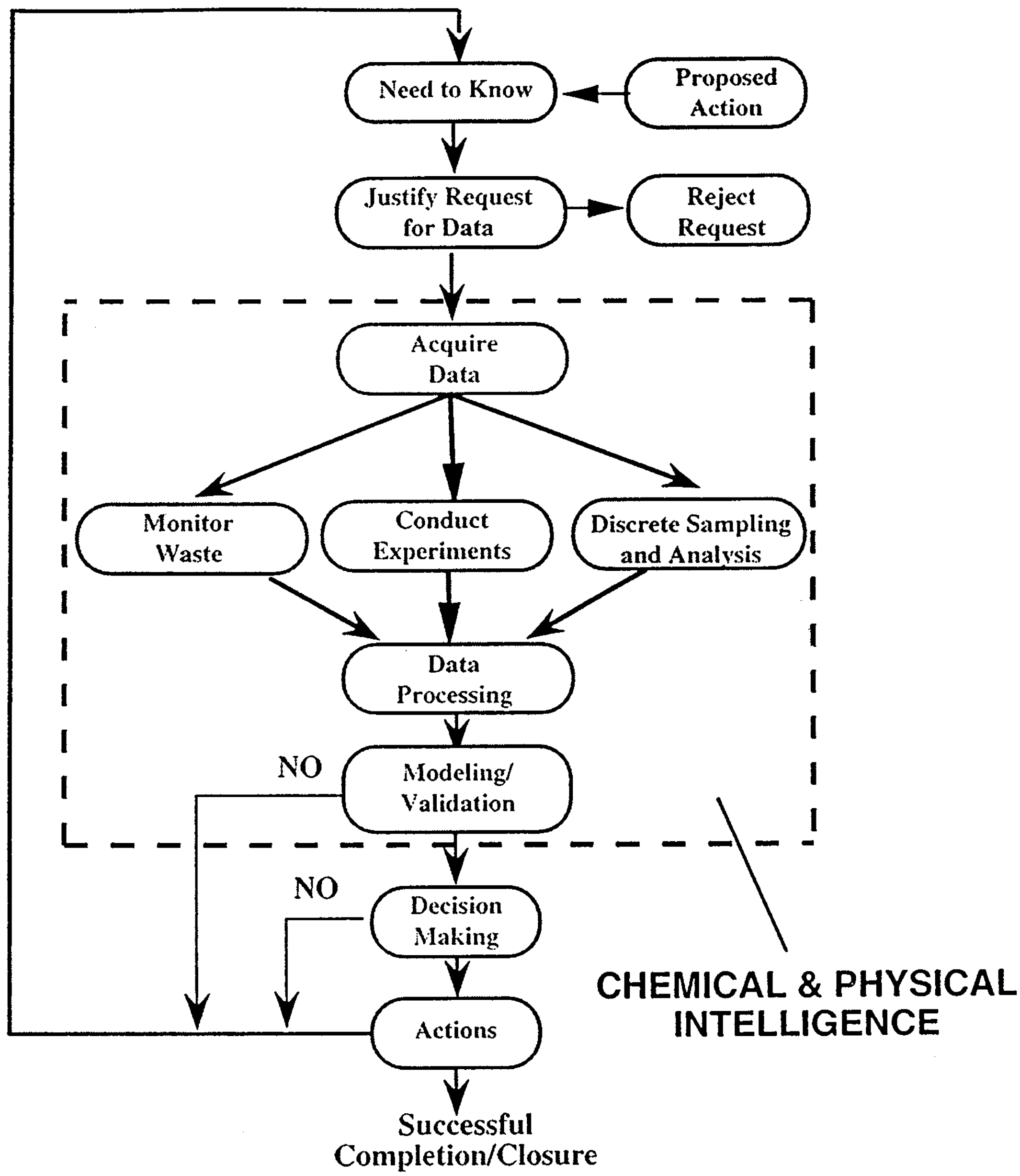

Fig. 2 Position of "Chemical & Physical Intelligence" in the environmental remediation scheme. Any request for characterization must be justified by the needs and intended outcome of the rational remedial action (from Ref. 5)