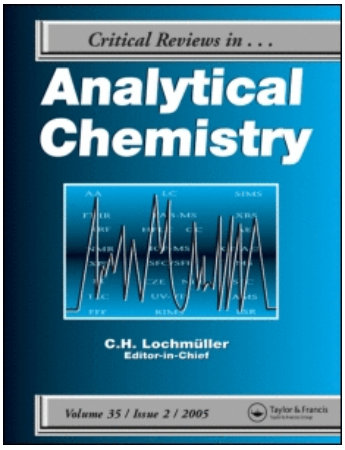

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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Online publication date: 03 June 2010

To cite this Article Janata, Jiří(1999) 'The Proper Place of Analytical Chemistry in Environmental Management', Critical Reviews in Analytical Chemistry, 29: 2, 155 — 162
To link to this Article: DOI: 10.1080/10408349891199301
URL: http://dx.doi.org/10.1080/10408349891199301

Critical Reviews in Analytical Chemistry, 29(2):155–162 (1999)

The Proper Place of Analytical Chemistry in Environmental Management

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ABSTRACT: Obtaining new information through characterizaton (chemical analysis) has its costs associated with it. These costs must be justified. It is argued that the value of any analysis, new chemical sensor, or a new analytical procedure for environmental management task is ultimately determined by its rational use. A formal procedure for justification of chemical characterization is outlined.

KEY WORDS: environmental restoration, chemical analysis, nuclear waste, hazardous sites.

I. INTRODUCTION

Environmental restoration and environmental management are complex tasks in which hard scientific facts blend with economic and even political considerations. Analytical chemistry occupies a central role in the assessment of environmental problems and in the clean-up schemes. In the operational sense, it is useful to think about analytical chemistry as a means of obtaining *chemical intelligence* that is analogous to military intelligence on a battlefield. Unfortunately, even the correct analytical information can be mismanaged, resulting in wasted resources and missed clean-up goals. In this article, I examine the position of analytical chemistry in environmental hazardous sites restoration, with specific references to the clean-up of nuclear waste at the Hanford site located in Washington State.

II. ESTABLISHING VALID CLEAN-UP STRATEGY

Large quantities of military nuclear waste exist at U.S. Department of Energy superfund sites.[1] The chemical and physical complexity combined with the inherent risk of a high level of radioactivity and the long half-lives of some man-made radionuclides make this clean-up an unprecedented environmental challenge. An even more disastrous environmental situation exists at the nuclear waste sites in the former Soviet Union,[2] where 1.7 billion curies of short- to long-lived radionuclides have been released into the environment. The estimated long-term ecological impact of the Cold War legacy is by far the most serious global environmental problem today.

The nuclear waste at Hanford exists in three general categories:[3] (1) contained waste

(tank waste; facilities, buried solid waste), (2) released waste (contaminated soil and groundwater); (3) stored materials (irradiated fuel, nonirradiated fuel, special nuclear materials, isolated Cs and Sr capsules). Each form of waste requires a specific remediation approach. The Pacific Northwest National Laboratory was charged to create a viable characterization component of the remediation strategy. A committee consisting of PNNL scientists and external experts prepared an extensive report[4] in which the role of characterization (i.e., analytical chemistry) was clearly defined. The findings of this report are used in this paper to define the proper role of analytical chemistry in the clean-up process. A misuse of analytical chemistry can happen anywhere. It results from undefined goals, incorrect technical strategy, and overall mismanagement. Although the examples given here relate to Hanford, the "abuse of analytical chemistry" can happen in any environmental clean-up.

A. Program-Based vs. Objective-Focused Characterization

Obtaining any piece of chemical intelligence always has a cost associated with it that can be quite considerable; for example, the total "cradle to grave" cost of the analysis of a core sample of radioactive waste extracted from a Hanford tank varies between 0.5 to 1.0 M$. It is reasonable to expect that such an expensive exercise would have some information value to the manager who requested it and that there was some operational reason to request it in the first place. In other words, such an expense should be justified in terms of the final objectives, that is, a demonstrated remediation of the waste of a particular tank. From this perspective, the typical management terms such as "cost", "justification", "final objectives" are linked to the technical activity of analytical chemists. Or are they? The answer to this question is relevant not only to the request for some routine analytical procedure, but it applies equally well to the request to develop a new analytical assay, a new chemical sensor or a new data evaluation algorithm, for potential future use.

The relationship between the cost and the value is well understood and respected in industry because it impacts directly the company's profit. The same cost-value consideration should also apply to any government-sponsored activity, although the profit is not the true motivation in that case. It is also an unfortunate fact that analytical chemists rarely think of their job in terms of cost analysis.

Let us look at the above-mentioned core sampling program and examine the reasons for doing it. The requirement to perform a certain number of core sample analyses is imbedded in the program-based strategy that has been defined by the upper DOE-EM management and other regulatory agencies.[5] It has been arbitrarily decreed that the tank contents cannot be treated until the "tanks have been characterized". The core sampling/analysis is the key part of such "characterization". Under this scheme the programmatic characterization objectives are met (and salaries and premiums are paid) if the specified number of core samples are analyzed in a given time period. More significantly, in this scenario the characterization is the determining and can become even disabling factor in the overall remediation program. To state it more directly, under this scenario characterization may become a legitimate reason for not initiating the waste remediation.

The notion that core sampling can characterize a tank is fundamentally flawed. The reason why this is so is evident from a schematic diagram of a typical waste tank shown in Figure 1. The largest of Hanford tanks are approximately 4000 m^3 containers. The waste is highly stratified and also laterally inhomogeneous mixture of inorganic compounds

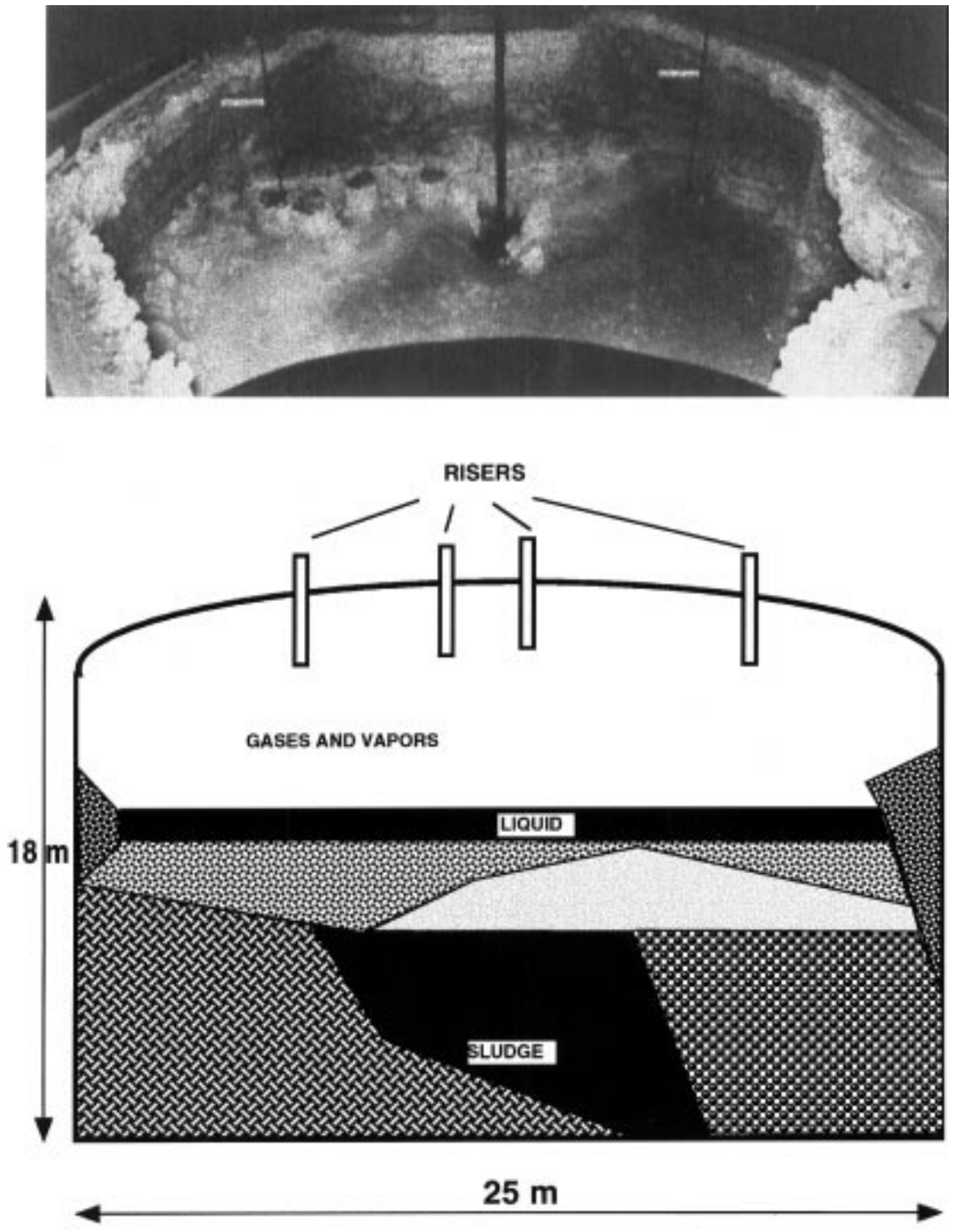

FIGURE 1. A wide-angle lens photograph of the interior of one of the Hanford tanks. Below is the schematic distribution of a tank waste. Each tank is different in terms of the chemical, physical, and radiological content of the waste that it holds.

and elements of nearly entire periodic table. In some cases, it also contains tons of solvents and other organic compounds. Moreover, it is alkaline and radioactive. There are 9 to 20 accessible ports in the dome of a tank that can be used to extract the core samples.

These ports are located in *fixed* positions. The typical number of prescribed core samples is 3 to 5/tank. Even an undergraduate student should recognize that sampling of solid, heterogeneous material through spatially fixed sampling points *cannot yield any useful information* about the *average* tank content. Therefore, the prerequisite tank characterization as the first step of the waste treatment cannot be met *a priori* because of the flawed sampling strategy. Yet, the prescribed number of core samples must be taken and analyzed at great cost, in order to satisfy the *programmatic characterization criteria* as required by the regulatory agencies. A "complete characterization" of a physically and chemically heterogeneous object is an undefined target. As such it can lead to an endless number of analyses that are limited only by the available characterization budget, not by their value. In this case the characterization is an activity motivated purely by the compliance and welfare objectives of the clean-up site, and not by the waste remediation goals themselves.

In contrast, the characterization should be an integral part of the remediation operation in the *outcome-focused* strategy. In that case it satisfies the value of information criteria, that is, *any request to obtain analytical information is justified by given, concrete operational objective*. This requirement removes the danger of doing characterization for its own sake or, even worse, making it an institutionalized impediment of the remediation progress. An example of justified characterization request under this paradigm would be an *opportunistic analysis* done during some remedial operation (e.g., transfer or treatment of the waste) targeting a specific compound or radionuclide (e.g., Pu).

The justification of a characterization request must be done in the context of *risk analysis*. The basic criterion of risk analysis is similar to the one used in the value of information paradigm. In risk analysis it is necessary to answer the question: "*what is the estimated cost of consequences of making a wrong operational decision?*".[4] The formal risk analysis exercise can be quite complex, particularly when hard-to-define parameters such as the value of human life or health risks in general are involved. Unfortunately, the chemical and physical nature of nuclear waste is such that it inevitably involves these considerations. Nevertheless, risk analysis is commonly done in most industrial operations. For example, *Structured Logic Diagrams* have been developed and used by the nuclear power-generating industry as the tool for solving complex multifaceted problems. They can be also used in the risk analysis involving environmental remediation.[4]

The position of the characterization in the overall operational scheme is shown in Figure 2. The proposed strategy is iterative. This means that on completion of one cycle the understanding of the problem (e.g., tank waste) becomes sharper, more focused. In that respect the characterization and the resulting clean-up steps are *parallel, not serial* activities. This is a key difference between the program-based and the outcome-based strategies as is schematically shown in Figure 3. One thing stands out immediately from the comparison of these two strategies: The intrinsic scientific merit of a valid characterization step becomes irrelevant with respect to its ultimate usefulness if it is mismanaged. In the best case the unjustified characterization is a waste of resources. In the worst case it becomes an impediment to the clean-up progress.

B. Another Specific Example of Abuse of Analytical Chemistry

Hanford site contains estimated 440MCi of radioactivity in many different forms of intermediately stored nuclear materials, contained and released waste. For comparison, the Chernobyl accident (1986) released

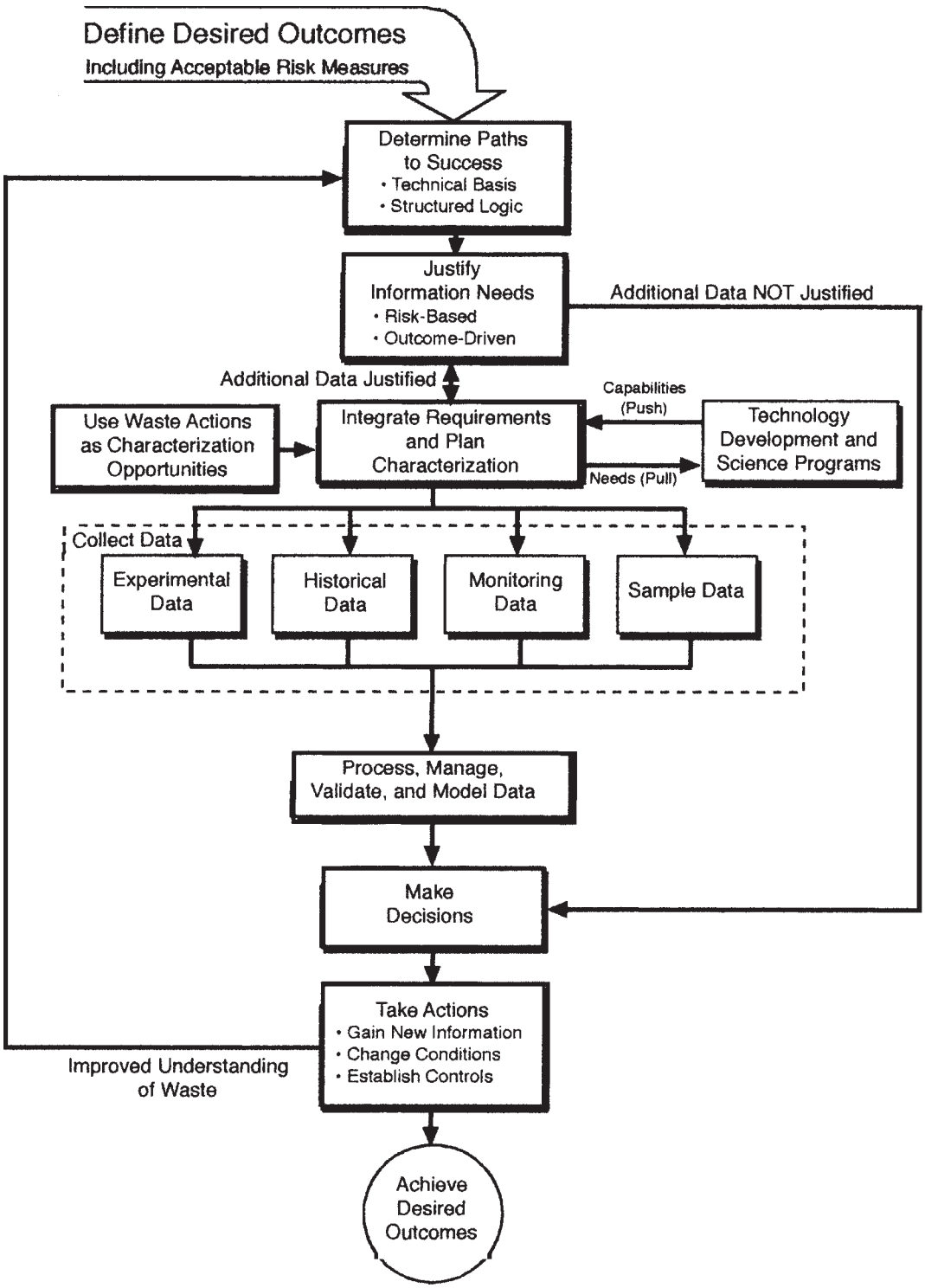

FIGURE 2. Role of characterization (defined by the dashed box) in tank waste remediation scheme. (From Ref. 4.)

approximately 50 MCi and during the Three Mile Island Accident (1979) only approximately 50 Ci was released. In order to manage and/or remediate this complex situation it is necessary to obtain chemical intelligence about distribution, location, and quan-

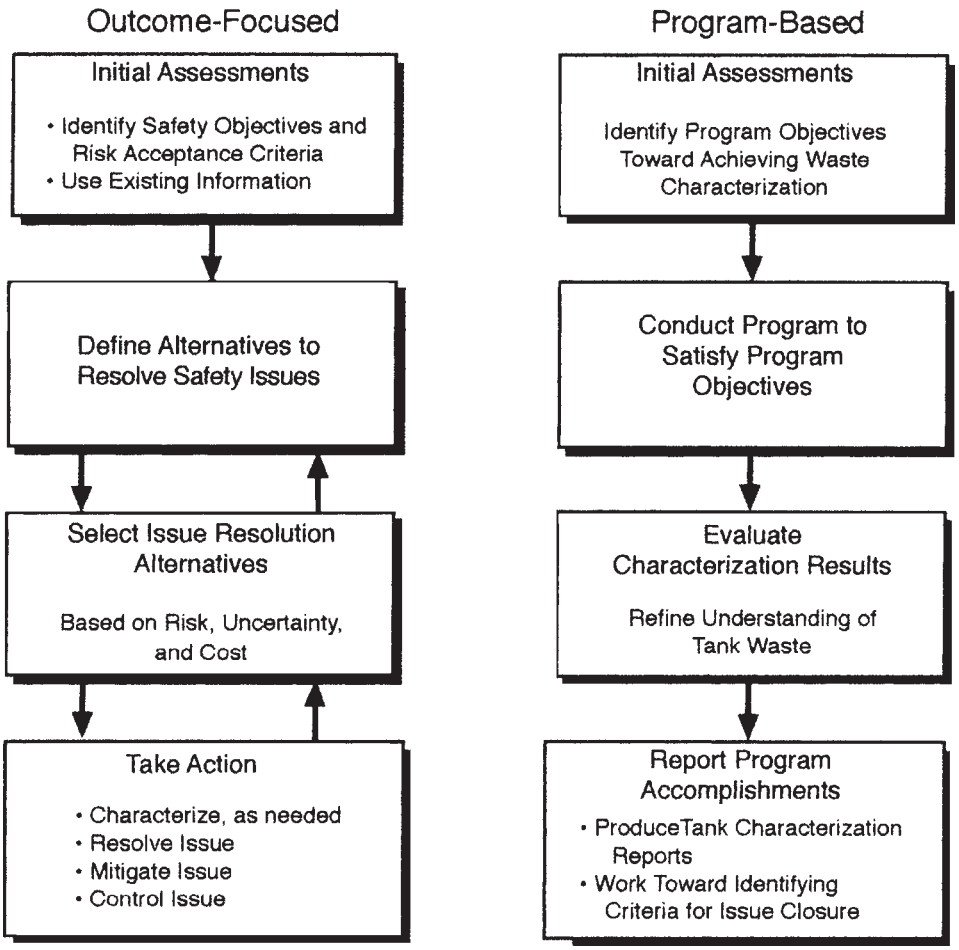

FIGURE 3. Comparison of the Program-Based and Outcome-Focused characterization strategies. (From Ref. 4.)

tities of various dominating radioisotopes such as Sr-90, Cs-137, actinides, Tc-99, etc. Development of an universal microanalytical, automated methodology that could be used under different conditions for analysis of radioactive waste seems to be a logical and legitimate goal. Such a project has been under development since 1994 at the Pacific Northwest National Laboratory in collaboration with the University of Washington.

Flow injection analysis (FIA) and its more recent cousin, sequential injection analysis (SIA), have been developed for many wet analytical processes.[6] They are remarkably flexible, compact, and inexpensive. For radiochemical analysis they can be combined with variety of radiochemical detectors such as liquid or solid scintillation counters, gamma spectrometers, or ICP-MS. A simple example of this methodology is illustrated by rapid analysis of Sr-90 in aged tank waste.[7] By this approach the troublesome problem of Sr-90 analysis, the ingrowth of Y-90, can be circumvented. In the manual format the usual, and not entirely satisfactory solution is the separation of Y-90 prior to the Sr-90 counting. In the SI format of the analysis the sample containing Sr-90 and other radioisotopes is first loaded through the sampling valve into the holding coil (Figure 4). In concentrated HNO_3 the Sr-90 is retained on the column, while the Cs-137

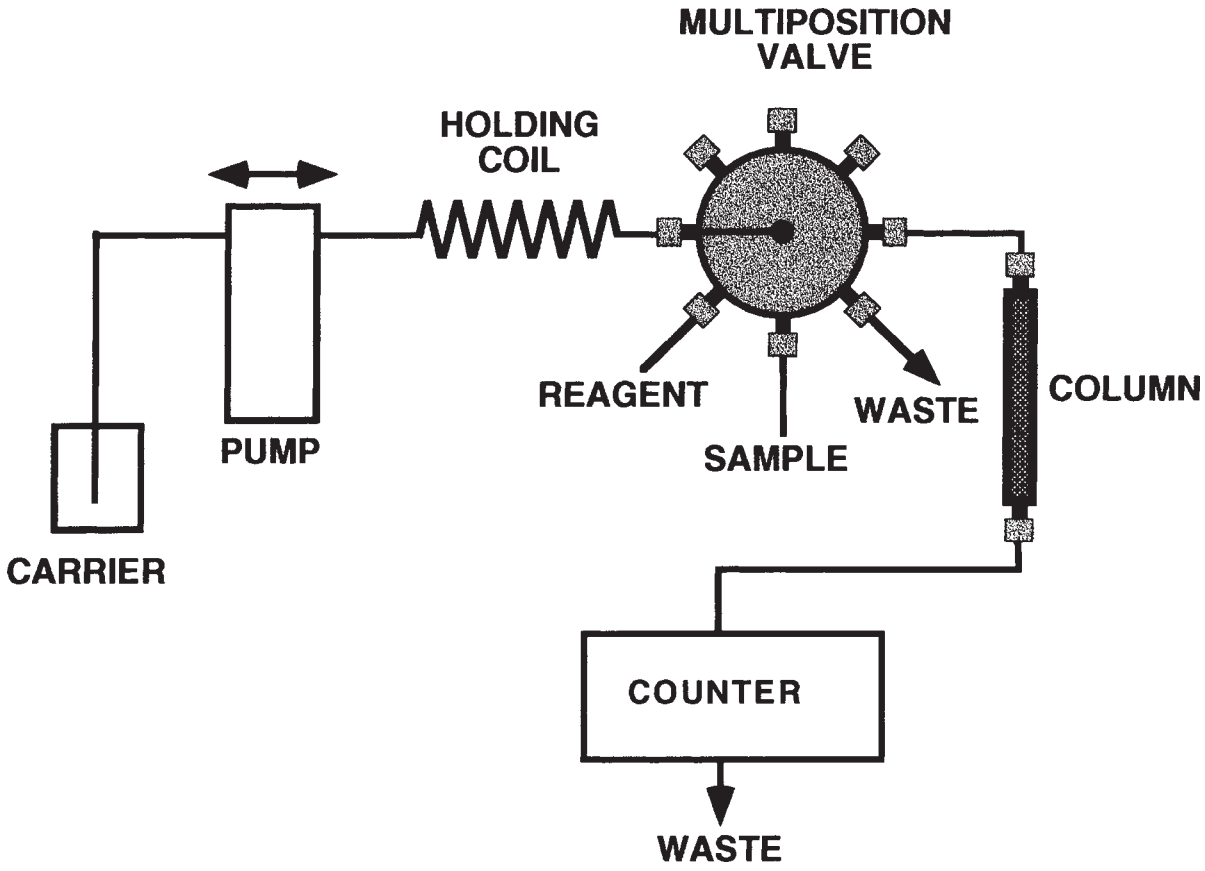

FIGURE 4. Manifold used for the SIA determination of Sr-90 in tank waste. (From Ref. 7.)

and Y-90 pass through. The adsorbed Sr-90 is eluted from the column with dilute nitric acid and passed through the β-scintillation counter into waste (Figure 5). For very low activity samples the flow can be stopped and the eluted zone can be counted for any desirable period of time. The new determination compares very favorably with conventional determination of Sr-90. It can be fully automated, it uses small amounts of sample and reagents, and it is much faster: 45 min compared with full 2 days for the manual separation. Because it handles a minute amounts of radioactivity, it can be performed in a low-level radiation zone as opposed to a hot cell required for the manual version of this analysis. The SI manifold can be configured in many different ways as required by the specific conditions of the analysis. Thus, procedures based on SI-radiochemical analysis have been developed also for actinides using on-column redox chemistry,[8] and Tc-99.[10] Despite these advantages, it has not yet been applied in the DOE remediation program. The reason is simple: it saves time and reduces the expenditure which is *not* in the interest of the program based strategy that supports the welfare paradigm of the Hanford clean-up.

III. CONCLUSIONS

One notable feature of this article is the relatively large number of references to various official reports. This is due to the fact that analytical chemistry, in the context of environmental restoration, is never an end in

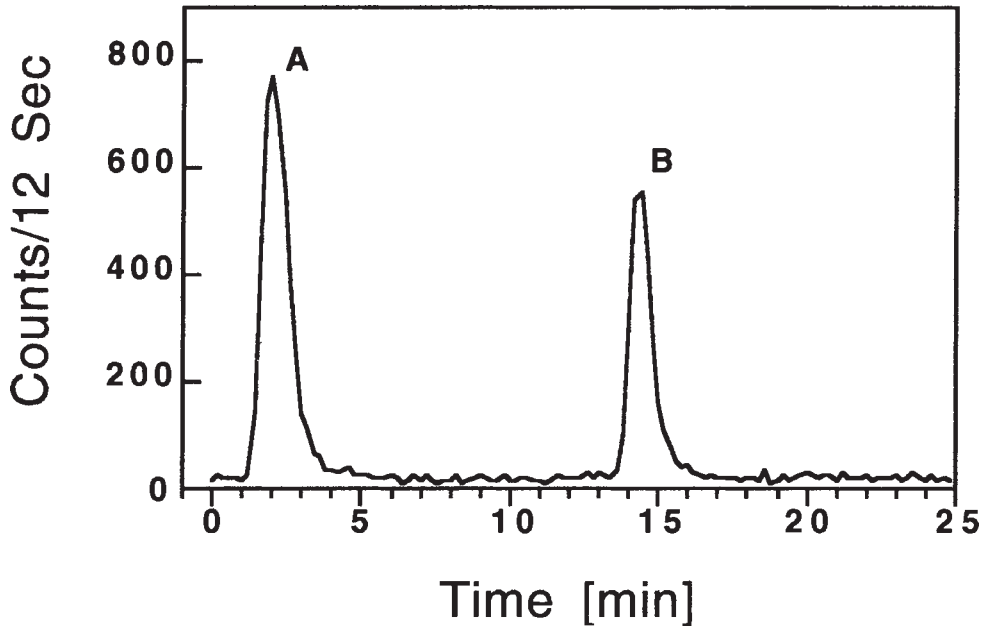

FIGURE 5. Example of Sr-90 (peak B) analysis in a real tank waste. Peak A is the activity due to the radionuclides other than Sr-90 that are eluted first, while Sr-90 is retained on the separation column. (From Ref. 7.)

itself. In some cases, the usefulness of analytical chemistry can be completely decoupled from its scientific merit resulting in wasted resources and impediment of the clean-up process.

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