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METHODS EVALUATION FOR THE CONTINUOUS MONITORING OF CARBON-14, KRYPTON-85 AND IODINE-129 IN NUCLEAR FUEL REPROCESSING AND WASTE SOLIDIFICATION FACILITY OFF-GAS

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IDAHO CHEMICAL PROGRAMS
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METHODS EVALUATION FOR THE CONTINUOUS MONITORING OF CARBON-14, KRYPTON-85, AND IODINE-129 IN NUCLEAR FUEL REPROCESSING AND WASTE SOLIDIFICATION FACILITY OFF-GAS

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ABSTRACT

The state-of-the-art for the continuous monitoring of ^{14}C, ^{129}I, and ^{85}Kr was evaluated. Published methodology and developmental programs at the Idaho Chemical Processing Plant are summarized. A sequential monitor is proposed where all forms of ^{14}C and ^{129}I are catalytically converted to a single form (CO_2 or I_2) and separated from interferences by selective permeation. Lastly, ^{85}Kr is monitored with a beta detector mounted in a flow chamber. A developmental program for extending the state-of-the-art is outlined.

SUMMARY

The continuous monitoring of ^{14}C, ^{129}I, and ^{85}Kr releases from reprocessing plant and waste solidification facilities is desirable from regulatory and process control viewpoints. The presence of high concentrations of NO_2 provides interferences for most methods currently employed. The separation of ^{14}C and ^{129}I from the NO_2 and ^{85}Kr in the sample stream is required for accurate monitoring.

The method proposed for development consists of the catalytic conversion of the ^{14}C to CO_2 and the ^{129}I to I_2. These species are then separated from possible interferences by selective permeation across thin membranes. The ^{85}Kr is counted directly since it does not suffer from significant interferences. The separated ^{14}C is counted with either a flowthrough proportional counter or an ionization chamber. A laser fluorescence method is proposed to detect the ^{129}I. A program is recommended to investigate the process chemistry of ^{129}I to determine the applicability of the continuous ^{129}I monitor to other nuclear facilities.

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I. INTRODUCTION

Nuclear fuel reprocessing and waste solidification facilities are required to monitor ^{14}C, ^{85}Kr, and ^{129}I releases to the environment. Three requirements must be fulfilled by any off-gas monitor for these nuclides:

1) Ability to establish compliance with government regulations and guidelines;
2) Ability to fulfill process control needs for maintaining compliance and identifying process upsets;
3) Compatibility with effluent stream characteristics, i.e., resistance to high NO_x and water vapor concentrations, or high temperatures.

To comply with government regulations and guidelines and to fulfill process control needs, the sensitivity and dynamic ranges shown in Table I are required. In addition, to function in the off-gas streams from the Idaho Chemical Processing Plant's (ICPP) Waste Calcining Facility (WCF), the proposed continuous monitors must not be affected by high concentrations of oxides of nitrogen, particulate activity, water vapor, and elevated temperatures. Figure 1 is a diagram of the WCF off-gas system with the available sampling points; Table II lists the sampling conditions at each of these points.

These radionuclides (^{14}C, ^{85}Kr, ^{3}H, and ^{129}I) with the minimal exceptions of ^{106}Ru, ^{125}Sb, and ^{119}Sn, make up the major gaseous components of the off-gas stream. Therefore, the ^{14}C, ^{85}Kr, and ^{129}I continuous monitors should be selective for the nuclide of interest in the presence of the other two isotopes. Table III shows the factors required to prevent ^{14}C, ^{85}Kr, ^{3}H, and ^{129}I from interfering with each other in the typical ICPP off-gas, factors required to reduce the possible combined interference to less than one percent. These separation factors were derived from typical activity ratios present in the ICPP stack gas.

The currently employed ^{14}C, ^{85}Kr, and ^{129}I monitoring methods are described and evaluated according to the above described criteria in the following pages. The most promising approach for the development of continuous monitors is also discussed, and a proposed development plan presented.

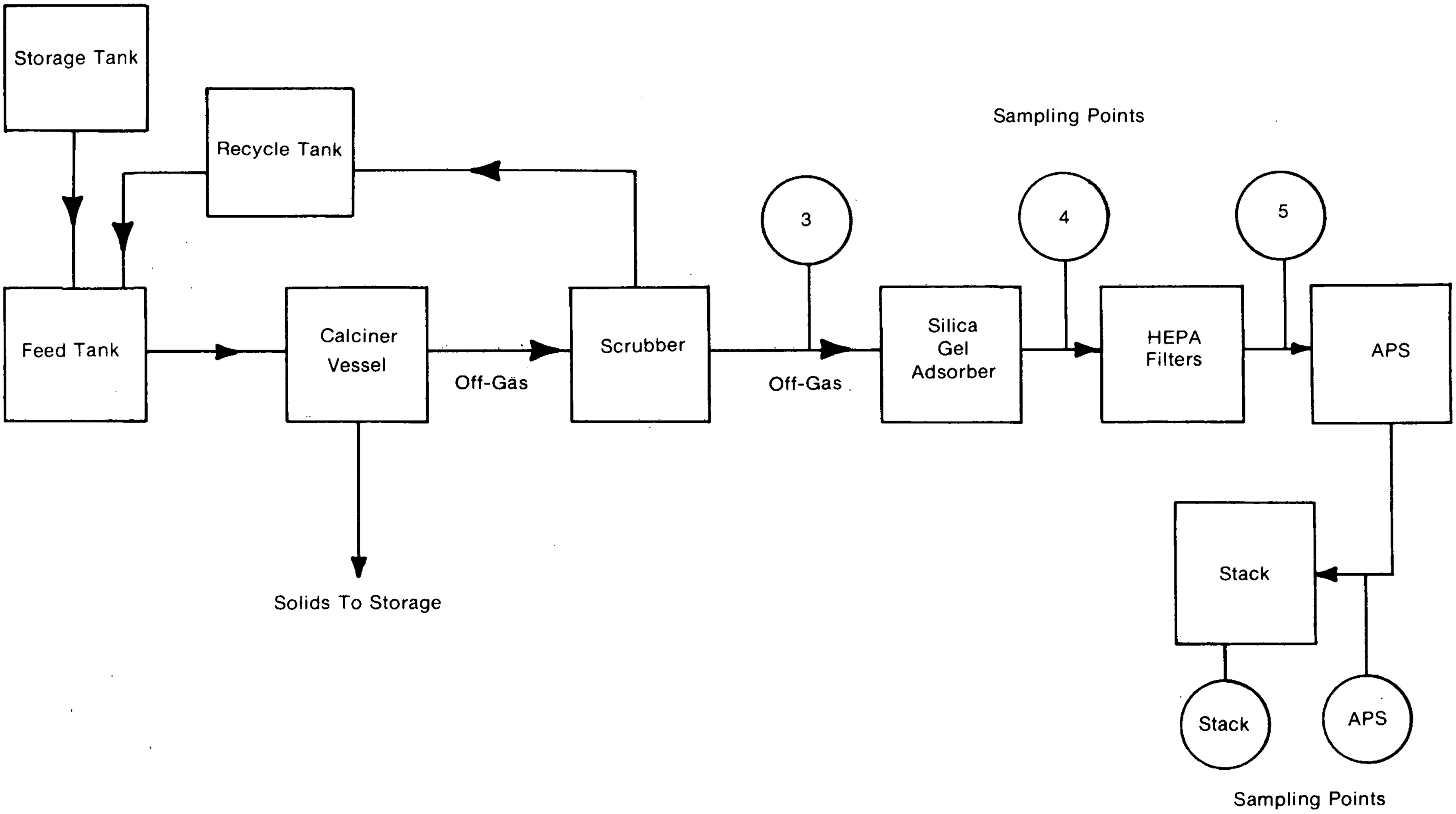

Figure 1. WCF Off-Gas System

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TABLE I

SENSITIVITY AND DYNAMIC RANGE FOR CONTINUOUS MONITORS

Isotope Monitored	Lower Limit of Detection μCi/cc	Dynamic Range μCi/cc
^{14}C	1×10^{-10}	$10^{-8} - 10^{-10}$
^{129}I	5×10^{-12}	$10^{-10} - 10^{-12}$
^{85}Kr	5×10^{-6}	$10^{-3} - 10^{-6}$
^{3}H	1×10^{-9}	$10^{-5} - 10^{-9}$

TABLE II

SAMPLING CONDITIONS AT WCF

Sample Point	NO_x ppm	Humidity % RH	Temperature °C	Maximum Sampling Time Minutes*
3	10 000	100	70	3
4	10 000	100	70	10
5	10 000	100	70	30
APS	7 000	12	50	Continuous
Stack	250	Ambient	20	Continuous

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*Limited by Particulate Activity.

TABLE III

REQUIRED SEPARATION FACTORS

Monitor	From ^{14}C	From ^{129}I	From ^{3}H	From ^{85}Kr
^{14}C	--	< 1	10^{4}	10^{7}
^{129}I	10 000	--	10^{6}	10^{9}
^{3}H	100	< 1	--	7800
^{85}Kr	< 1	< 1	< 1	--

II. CARBON-14 ANALYTICAL METHODOLOGY

The nuclear transformation: $^{14}N(n,p)^{14}C$ is the primary formation reaction for ^{14}C. The reaction may occur in the atmosphere with neutrons from cosmic ray interactions, nuclear weapon detonations, or operating reactor fuel rods. The benchmark for assessment of environmental ^{14}C levels is 1952, since that year marked the beginning of atmospheric testing of high yield weapons.[1] The best available estimates are about 14 disintegrations per gram of carbon, equivalent to 10^{-12} μCi/cc air (at 315 ppm CO_2).[2] The maximum specific activity in the northern hemisphere, attained in 1962, was about twice that due to natural ^{14}C alone.[3]

The maximum allowable concentration in air (MPC_A) for ^{14}C, whose half-life of 5730 years makes it an essentially permanent environmental contaminant,[2] is 5×10^{-5} μCi/cc for controlled areas and 1×10^{-6} μCi/cc for non-controlled areas.[4] Implementation of the philosophy of "as low as reasonably achievable" demands a knowledge of release activity levels associated with the nuclear fuel reprocessing industry.

The measurement of ^{14}C is difficult because it decays with the emission of low energy (β_{max}= 0.150 Mev) beta particles without any accompanying gamma radiation. There are three additional difficulties associated with the continuous on-line monitoring of ^{14}C: (1) There are interferences from other typical stack gas constituents, primarily ^{85}Kr and ^{3}H, which are not readily separable from the ^{14}C. The continua of higher energy beta-emitting nuclides such as ^{85}Kr mask the ^{14}C spectrum. (2) Waste solidification facility off-gas is extremely corrosive to many monitor materials of construction due to high NO_x concentrations in the stack gas. (3) Many detectors, otherwise suitable, are also sensitive to the high and variable ambient gamma field which may be present.[5]

Present and proposed methods for continuous ^{14}C monitoring consist of two independent stages. The first stage separates the ^{14}C from interfering nuclides, NO_x, and other gas stream constituents harmful to the detector. The second stage is the detector which counts the separated ^{14}C.

1. Separation Techniques

The techniques of interest to continuous monitoring are based on separation and recovery of ^{14}C as $^{14}CO_2$. Light water reactor studies[6,7] showed as much as 80% of the ^{14}C is present as oxidizable forms (CO, CH_4, C_2H_6, etc.). Although such high proportions of reduced carbon species are not documented for fuel reprocessing facility off-gas, a requirement of any on-line ^{14}C monitor is inclusion of an oxidizing system to assure that all ^{14}C is in the fully oxidized state (CO_2). The resulting CO_2 may be separated from the gas stream by adsorption onto a molecular sieve, by precipitation as an insoluble carbonate salt, or by permeation through a suitable membrane. These approaches are considered separately below.

1.1 Molecular Sieves

Molecular sieves are crystalline metal alumina-silicates which form small cavities known as sodalite cages. These cavities are a few angstroms (Å) in diameter with six accessible sides. One or more cations in the molecular structure can partially block the face of the cage, however. The size of the blocking cation then determines the size of the "door" to the sodalite cage. When sodium is the blocking cation, the door is approximately 4.2 Å wide. The crystalline structure of this sodium form is represented chemically by the following formula:[8]

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \text{ x } H_2O$$

The capacity of molecular sieves is only weakly dependent upon temperature in the region below 80°C. The stability of the molecular sieve capacity compared to other adsorbents is believed to be caused by ion dipole links formed between the adsorbate molecules and the cations on the surface of the sodalite cages. This strong attractive force causes preferential adsorption of polar molecules, such as CO_2.[5,8]

Use of molecular sieves for CO_2 recovery is applicable to semicontinuous, but not continuous monitoring. After a sampling period, the sieve is heated in a tube furnace for about 4 hours at 350°C with a dry He purge to remove adsorbed CO_2. The CO_2 is expanded into a bulb of calibrated volume and its pressure measured, allowing calculation of the recovered CO_2 mass.[9]

The principal drawback to using a molecular sieve in an automated, semicontinuous application is its lack of specificity. Polar compounds in the stack gases, such as water vapor, would also be adsorbed. Major interferences would be HTO, a radiochemical interference, and NO_x, which would degrade counter performance. Samples desorbed from molecular sieves at the ICPP have an HTO : CO_2 : NO_x ratio as high as 100:5:1.[5] The interferences are unacceptably high for use in a continuous or semicontinuous monitor.

1.2 Carbonate Precipitation

Carbon dioxide may be separated and recovered by passing the sample gas stream through a bubbler system containing an alkali or alkaline earth hydroxide solution. The resulting carbonate may be precipitated as barium or calcium carbonate[10] and counted as a suspension by liquid scintillation or directly with a surface barrier derector. The carbonate may also be acidified and the released CO_2 reacted with a liquid scintillation cocktail containing ethanolamine.

There are several drawbacks to this procedure. First, it is not amenable to an automated continuous monitoring system since sufficient carbonate must be generated to form a filterable precipitate. This method, requiring 2-week sampling times, is in use at the present ICPP stack monitor. Second, the method is not quantitative. Placement of a second bubbler in series at the ICPP stack showed some CO_2 does not react in a $Ba(OH)_2$ system.[11] Furthermore, barium carbonate is slightly soluble, so some of the salt is lost in subsequent handling. For these reasons, the carbonate precipitation procedure is not suitable for a continuous monitoring system.

1.3 Membrane Permeation

The separation process which presents the greatest promise for continuous on-line monitoring of ^{14}C is membrane permeation. This method employs polymeric tubing through which selected material (CO_2) quantitatively diffuses while other stack gas constituents remain in the process stream.[11,12,13] A typical separation device consists of many thin-walled polymeric tubes mounted in a common header and sealed into an outer shell. A schematic diagram is shown in Figure 2.

A process stream constituent continuously diffuses through the tubing wall according to the equation:[12]

Flux of constituents = $K P \Delta p$

where K = geometry factor, a function of tubing length, wall thickness, and radius;

P = permeability of the polymer to the diffusing species, a function of membrane material, nature of the diffusing species and temperature;

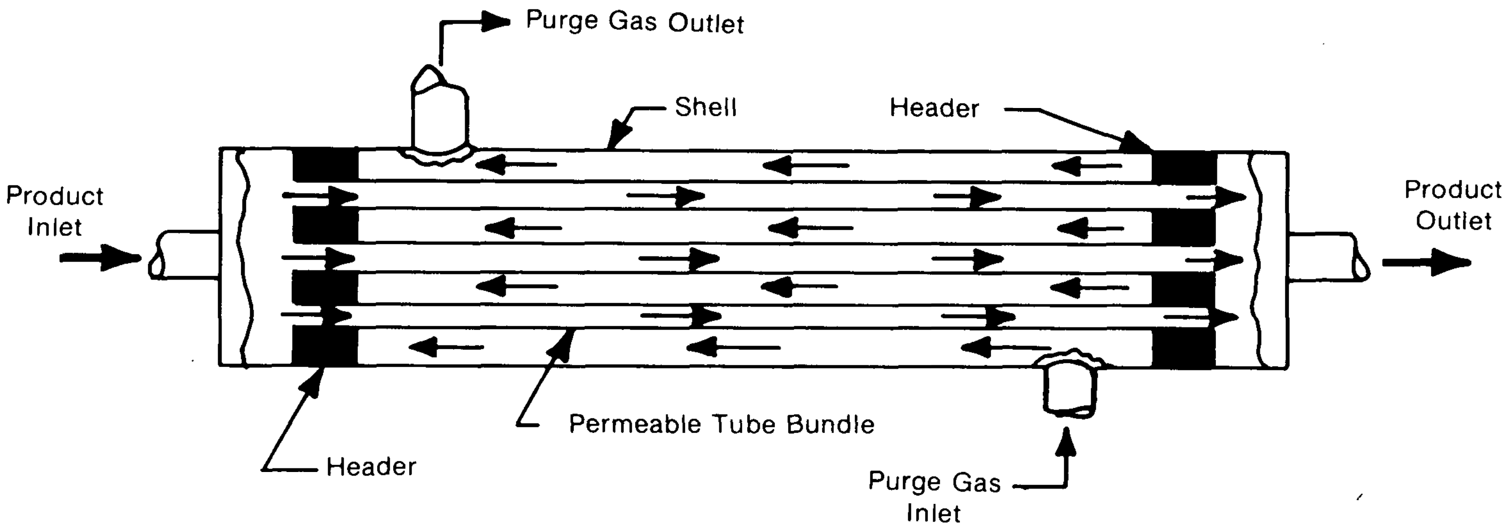

Figure 2. Schematic Diagram of a Permeation Distillation Device

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Δp = difference in the inner and outer bulk partial pressures of the diffusing species.

Materials are available for which P, the permeability, is uniquely high for H_2O and a permeation device was proposed for use in a continuous tritium monitor.[5] Although materials permeable only to CO_2 are not available, a permeation device selective for CO_2 is possible by use of a purge gas of proper composition. Such a purge gas would model the sample stream except that it would be CO_2-free. Thus, diffusion rates for all process gas constituents would be zero ($\Delta p = 0$), and the diffusion rate for CO_2 would be maximized (Δp = maximum). Gases such as Kr and H_2O used in making a proper purge gas would be present as nonradioactive isotopes only, thus eliminating radiochemical interferences.

Preliminary laboratory data from evaluation of this method for tritium separation showed $^{14}C/^{3}H$ separation factors of >200 are possible. These experiments also showed that the device is not adversely affected by several months of operation at NO_x concentrations over 10 000 ppm.[5]

Therefore, permeation is the method of choice due to its quantitative separation of CO_2 from interfering radionuclides and its compatibility with NO_x streams. In addition, the method seems suitable as the basis of a series of on-line monitors, sequentially separating and assaying ^{3}H, ^{14}C, and ^{129}I, described in Section IV.

2. Detection Methods

A review of detection methodology applicable to counting low-energy beta emitting gases was done by Fernandez and Girton.[5] Their conclusions are applicable to ^{14}C monitoring.

2.1 Ionization Chamber

The principle of operation of an ionization chamber relies on the property of energetic charged particles to produce ion pairs. In the simplest ionization chamber, the charged particles enter a gas-filled gap between two charged electrodes. The positive and negative ions formed by passage of the charged particles are accelerated by the electric field established between the electrodes. The resulting current then is measured and is directly proportional to the number of charged particles passing through the chamber.

Although ionization chambers are the most sensitive detectors for radioactive gases,[5] they lack specificity, responding to any ionizing event within the chamber. The ionization events may be caused by radiochemical interferences in the sample or ambient radiation fields. The most common method of minimizing the effect of ambient gamma fields is to use a second, sealed ionization chamber from which the sample is excluded. This second chamber physically surrounds the sample and acts as a measure of the gamma background. A typical chamber is shown in Figure 3. The ^{14}C signal is represented by the difference in ion current between the sealed chamber and the flowthrough detector.

The drawback to this method is that spurious background events are not eliminated, but identified as background. Since the detection limit of a radiation detector is directly proportional to the background, the sensitivity of an ionization chamber would be a function of the gamma field to which it is exposed. Therefore, when an ionization chamber is operated in a varying gamma field, as is common at reprocessing plant stacks, the detection limit would also vary. A varying background and detection limit is unacceptable for a continuous monitor. If the problem of radiochemical interferences could be solved by an efficient separation method and the detector well shielded, then the ionization chamber would be the detector of choice due to its greater sensitivity.

2.2 Liquid Scintillation Counters

Liquid scintillation, although usually applied to radioactive liquids, may be applied to gaseous monitoring. The theoretical mechanism of liquid scintillation involves intimately mixing the sample (usually as a carbonate salt) with a scintillator. The scintillator is typically a fluor (usually an oxazole or oxadiazole capable of deexciting with the emission of a photon) dissolved in one or more solvents. The energy from the ^{14}C betas is absorbed by the solvent and transferred to the fluor molecules. The fluor molecules deexcite by the emission of photons. The number of photons is directly proportional to the energy dissipated. These photons are detected by an array of photomultiplier tubes whose output is proportional to the number of photons detected. In this manner it is also possible to perform energy discrimination.

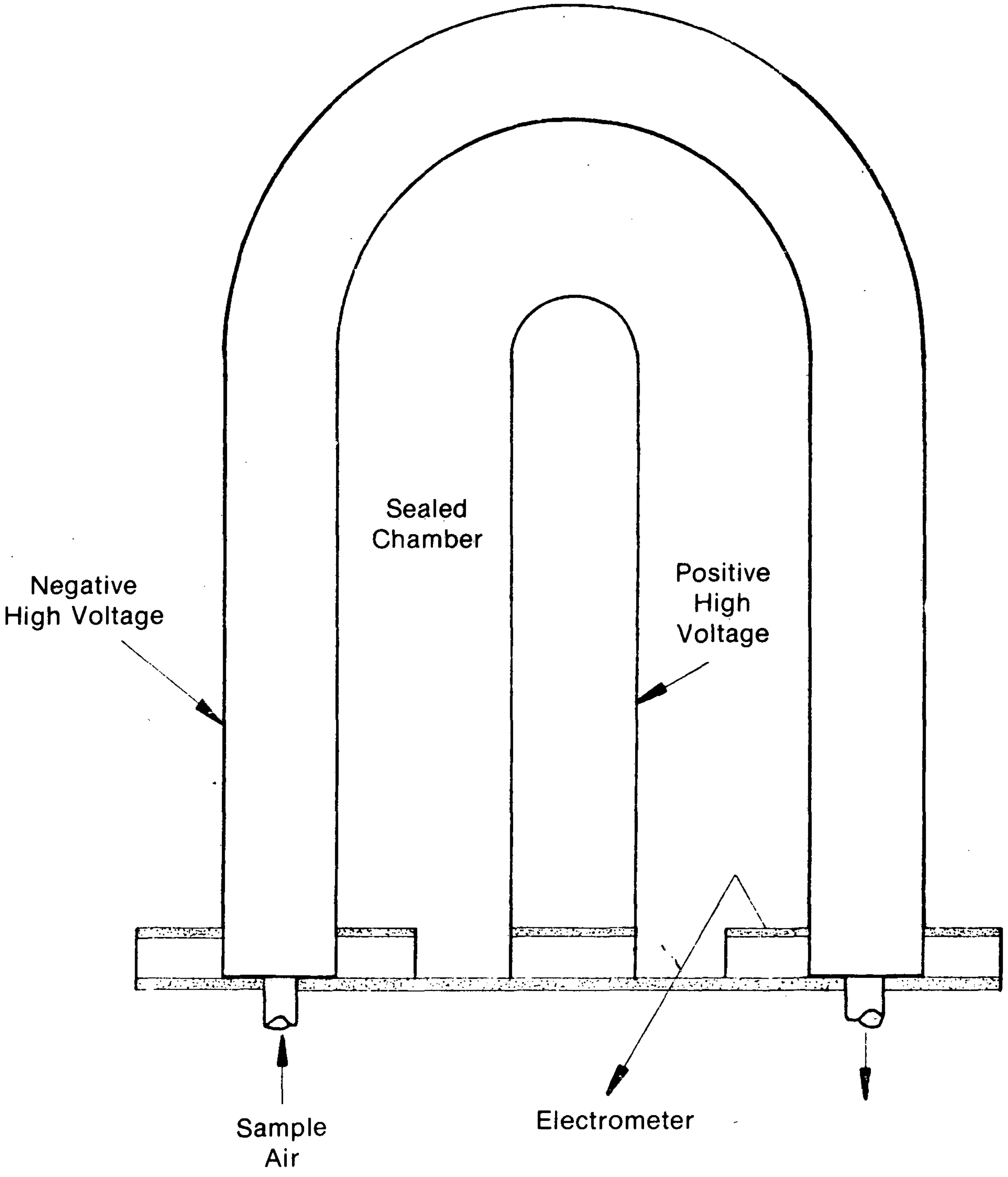

Figure 3. Ventilated and Sealed Ionization Chamber

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There are two major shortcomings of the liquid scintillation method: 1) the lack of a suitable separation method to precede the counting of the sample; liquid scintillation has most commonly been used with the carbonate precipitation with the concommitant drawbacks already described. 2) the prohibitive operating costs: at present ICPP CO_2 concentrations (300-900 ppm), a minimum scintillator flow of 1 mL/min would be required. At present prices of suitable scintillators, the annual cost of scintillators alone would exceed $10,000. For this reason, liquid scintillation as a detection method for a continuous monitor is economically infeasible.

2.3 Solid Scintillators

Since costly scintillation methods are currently the only practical approach to monitoring liquids for low-energy beta emitters, there has been increasing interest in developing solid scintillators as an economic alternative to liquid scintillation. The drawbacks to solid scintillators are their sensitivity to both gamma radiation and non-^{14}C beta particles.

One original method of eliminating gamma background while simultaneously discriminating against high-energy beta activity is to use a CaF_2 (Eu)/CsI-(Tl) phoswich detector. The phoswich detector is composed of a thin CaF_2(Eu) crystal optically coupled to a CsI(Tl) scintillator. The signal from the entire detector is generated by a single photomultiplier tube whose output is triggered by events occurring in one or both of the scintillators.

It is possible to determine the origin of an event by pulse shape analysis since the rise time of pulses originating in either phosphor is characteristic of the crystal. When a background gamma ray is incident upon the thin CaF_2(Eu) crystal, it will deposit energy in both scintillators. By operating the CsI(Tl) detector in anticoincidence with the CaF_2(Eu), gamma caused events are not counted as ^{14}C pulses. This background elimination capability makes the phoswich detector attractive for on-line monitoring of reprocessing plant stack gases. The drawback to this detector is that it has a low counting efficiency for ^{14}C. While not the method of choice in this proposal, it shows sufficient promise to be considered as a viable alternative.

2.4 Proportional Counters

The theory of proportional counters is similar to ionization chambers with the exception that they are operated at considerably higher voltages and must be operated with a counting gas, typically an argon-methane mixture. As a result, a charged particle passage does not cause an immediate avalanche or discharge, but a pulse is generated as the ions migrate toward the anode, causing an avalanche only in the immediate vicinity of the anode. The size of the pulse is proportional to the number of ion pairs formed in the original event, i.e., proportional to the energy of the beta particle.

Gas flow proportional counters combine the advantage of high counting efficiency with pulse height discrimination. The reduction of response to background gamma radiation is achieved by either a guard ring of Geiger-Müeller tubes or a second counter which is electrically separated from the original tube by a wire grid. An external gamma ray would penetrate both chambers; by use of appropriate electronics, these coincident signals are not counted. Both beta and gamma compensation may be achieved by operating the outer counter in anticoincidence with the inner chamber.

Therefore, the gas flow proportional counter appears to be the most promising detector, and is the primary counting method explored in the proposed program. The integrated monitor with its relationship to the ^{85}Kr and ^{129}I monitors is presented in Section V.

III. KRYPTON-85 ANALYTICAL METHODOLOGY

The Environmental Protection Agency has established standards requiring the total quantity of ^{85}Kr entering the general environment be less than 50 000 curies per gigawatt-year of electrical energy produced by the nuclear fuel cycle.[15] The primary methods of analyzing stack gases for ^{85}Kr involve removing the gross particulate activity from the sample stream and flowing the sample into a counting chamber containing a gamma or beta detector. The general approaches taken to development of these monitors have paralleled ICPP programs.

Originally, the ^{85}Kr ICPP stack monitor consisted of a 7.5-cm by 7.5-cm NaI(Tl) scintillation detector. The detector was positioned in an 8-L inverted Marinelli-type beaker. The detector assembly was then placed in a 5-cm thick lead barricade located at the base of the stack. Filtered sample air was continuously taken from the stack, purged through the detector housing, and returned to the stack. Sample flow rates were controlled to maintain isokinetic conditions.

Ancillary equipment included a single channel analyzer (SCA) and a teletype with a paper tape punch. The SCA was set to monitor the 514 KeV ^{85}Kr gamma ray. Data were reduced by computer processing the paper tapes to obtain the μCi/sec release rates.

Due to a high background-to-signal ratio, the count rates were frequently at or near the lower detection limit of the system. Consequently, a second system was designed and installed to improve the system.

This system filters the sample stream with a 4.7 cm Gelman A/E filter. The sample stream is then passed through a second A/E filter, TEDA impregnated charcoal, a third filter, a bed of silver zeolite (10-16 mesh) and a fourth A/E filter. The sample is then dried by a bed of silica gel before introduction to the detector chamber. This sample train has proven effective in eliminating interferences from the volatile gases ^{129}I, ^{125}Sb, and ^{106}Ru, as well as the semi-volatiles ^{144}Ce, ^{137}Cs, and ^{134}Cs, which may penetrate the first glass fiber filter.

The detector currently being used is a flowthrough system that detects the ^{85}Kr beta (β_{max} = 0.67 MeV). The flow chamber is 2.5-cm-diameter by 3.8-cm-deep. A 2.5-cm-diameter silicon surface barrier detector is mounted in the base of the chamber and protected from possible contamination by a 0.1-mm-thick mylar window. This sample chamber and detector are contained in a cylindrical lead barricade with an outside diameter of 9.5 cm and a height of 14.6 cm. The walls of the barricade are 2.5-cm-thick. A pressure transducer and thermocouple continually measure the pressure and temperature within the chamber. The detector is connected to a single channel analyzer set to discriminate against electronic noise and any low-energy interferences such as ^{3}H and ^{14}C. Pressure, temperature, stack flow, and count rate signals are received by a microprocessor. From this data, the sampling interval and integrated release are calculated and the results printed on a teletype.

This system was operable during most plant operations in 1977. Three major deficiencies were identifed: 1) background counts were not constant during plant operations; 2) electronic signal noise produced spuriously high results; 3) room temperatures often exceeded the tolerance of the microprocessor and associated electronics. Therefore, a developmental program was initiated and the performance of the derived solutions recorded during a plant run from July to October 1978 (Run 36).

The gradual increase in background during a plant run was thought to be caused by the permeation of the ^{85}Kr in the sample stream into the necessary polyethylene tubing. The polyethylene tubing was to eliminate ground loops within the flow system. Therefore, measurements were made to quantify the observed background drift and to determine whether the permeation phenomena was of sufficient magnitude to account for the observed drift. The background drift was quantified by introducing a measured amount of ^{85}Kr standard into the monitor and observing the change in background after the ^{85}Kr was purged from the system. The calculated permeability of polyethylene tubing to account for this effect would be of the order of $2\text{x}10^{-7}$ cm^3 (STP)/$\text{cm}^3\cdot$mmHg. Additional experiments are planned to refine this measurement, but the implication is to minimize the use of polymeric materials in any ^{85}Kr monitor. It was possible to limit the bias from this effect to less than one percent during Run 36.

The effects of NO_x, water vapor, and NO_x plus water vapor on the background and counting efficiency of the ^{85}Kr monitor were investigated. No significant effects were observed.

Three major sources of electronic noise were identified and eliminated once Sorenson transformers were installed to eliminate power supply fluctuations. The first two sources of noise were the thermocouple and the pressure transducer mounted within the counting chamber. Both devices created intermittent ground loops that spuriously increased the background by 0.5-10 cps. These ground loops were eliminated by mounting the pressure transducer and thermocouple immediately upstream of the counting chamber. The pressure transducer and thermocouple were electrically isolated from the counting chamber by short pieces of polyethylene tubing. The amount of polyethylene used was minimized as indicated by the permeation experiments. The third source of electrical noise was vibration of the connectors between the detector and preamp caused by upstream sample changeout or normal plant noise. This source of noise was eliminated by mounting the connectors in hard rubber. During Run 36, no spikes attributable to electronic noise were observed.

The data analysis to determine the precision and accuracy of the monitor consisted of integrating the curies of ^{85}Kr measured during each batch dissolution and comparing this value with the calculated release assuming an average cooling period. The observed release/calculated release ratio for the 32 batches analyzed was 0.92 ± 0.24 (1σ). The ratio of 0.92 is in good agreement with the ratio of 1.00 that corresponds to perfect agreement. The uncertainty of 0.24 is larger than expected, but may be attributed to the appropriateness of the constant cooling period assumption. In practice, variability in the cooling period may contribute an additional 18% uncertainty.

Possible alternate detectors for ^{85}Kr include ionization chambers, solid scintillators, and proportional counters. The higher concentrations of ^{85}Kr minimize the necessity of discriminating against the ambient background at fuel reprocessing plant stacks. For this reason, proportional counters have no advantage over the more sensitive ionization chamber.

During the last four final batches of the study period, a 20-L ionization chamber was installed to simultaneously measure the ^{85}Kr releases and compare its performance to the surface barrier detector. The larger volume eliminated much of the fine structure of the releases, so it was thought to be a more reliable measure of the total release. The ratio of the release measured by the ionization chamber to the surface barrier detector was 1.18 ± 0.03, the uncertainty representing one standard deviation of the individual batch ratios. The low relative standard deviation of this ratio is an additional indication that the variability in the measured ^{85}Kr: calculated ^{85}Kr ratio of the surface barrier detector is not an inherent instability of the ^{85}Kr monitor. The signal-to-noise ratios of the two instruments were determined to be roughly equivalent.

From these comparison studies, it appears that sensitivity is not the limiting consideration, but greater stability is required. Insufficient studies are reported in the literature to determine if solid scintillators will perform better than ionization chambers or the surface barrier detector. Therefore, detector comparison studies are proposed in the development of the integrated monitor described in Section V.

IV. IODINE-129 ANALYTICAL METHODOLOGY

The discharge of radioiodine to the environment from nuclear fuel reprocessing plants is of particular interest due to the ability of iodine to enter the food chain and subsequently concentrate in the human thyroid. Iodine-129 is the isotope of interest during fuel dissolution and waste solidification since its 17-million-yr half-life makes ^{129}I a permanent contaminant of the environment. During normal operations of nuclear power stations, negligible amounts of ^{129}I are discharged to the environment.[15] Cochran, et al.[16] found significant quantities of ^{129}I were emitted via the stack at the Nuclear Fuel Services' reprocessing plant at West Valley, New York during fuel dissolution. Stack monitoring at the Idaho Chemical Processing Plant has not detected significant ^{129}I releases during fuel dissolution, but detectable amounts were released during waste solidification. These results contain two important implications for the continuous stack monitoring of ^{129}I. First, the chemical species of the emitted ^{129}I may not remain constant during chemical processing nor be predicted when different processes are used, thus invalidating any separation and/or detection method dependent upon single iodine species. Secondly, the effective control of ^{129}I emissions would be aided by knowledge of the factors affecting iodine volatility.

In 1977, a program was started at the ICPP to determine the quantities and species of the ^{129}I in both liquid and gaseous streams. Some of the results and plans of this program are reported in the following sections.

1. Liquid Iodine Analytical Methodology

To confirm that the ^{129}I in the reprocessed fuel elements remains primarily in the dissolution liquor and is not volatilized until the waste solution is solidified, it became necessary to develop a method of analyzing the waste solutions for ^{129}I before solidification. A successful analytical method in this application must:

1) be adaptable to remote handling procedures;
2) provide decontamination factors of greater than 10^7 for ^{137}Cs;
3) be able to tolerate concentrations of fluoride as high as $3.5\underline{M}$, Hg as high as $0.05\underline{M}$, and Al as high as $0.79\underline{M}$.

The first requirement was satisfied by several current solvent extraction methods.[18,19] The separation procedure developed by Flynn[17] was selected for modification since the effect of milligram quantities of aluminum and mercury was reported as minimal. The modified procedure is presented in the Appendix. Table IV shows the decontamination factors achieved with this procedure. These decontamination factors were sufficient to allow the separated samples to be counted as aqueous solutions on a hyperpure germanium low-energy photon spectrometer (LEPS). The 29 KeV Xe X-rays and 40 KeV ^{129}I gamma rays were integrated to determine the quantity of ^{129}I separated.

TABLE IV

MINIMUM DECONTAMINATION FACTORS

Nuclide	DF
^{144}Ce	$> 3.9 \times 10^5$
^{60}Co	$> 1.2 \times 10^4$
^{154}Eu	$> 2.6 \times 10^5$
^{125}Sb	$> 2.5 \times 10^5$

2. Gaseous Iodine-129 Analytical Methodology at ICPP

In addition to the liquid sampling at the ICPP, off-gas streams and stack effluents are analyzed to complete the ^{129}I mass balance around the WCF. Due to the NO_x concentrations in the WCF off-gas streams, special sampling procedures were required.

The ^{129}I samples are routinely taken at the 27.5-m level of the stack by drawing 1.1 L/min through a 40-g TEDA (tetraethylenediamine) impregnated charcoal bed. Prior to going through the bed, the sample stream is filtered with a 4.7-cm fiberglass filter. The charcoal bed is followed by a 55-g silver exchanged Type 13X zeolite bed. The charcoal bed is analyzed every two weeks by counting directly on the LEPS.

To verify the quantitative retention of iodine on charcoal under ICPP stack conditions, two types of backup beds are used to detect breakthrough of the iodine samples: 1) a charcoal bed identical to the original sampler; 2) a backup bed containing 55 g of silver zeolite. Neither backup bed contained detectable amounts of ^{129}I, indicating quantitative retention of iodine by the first charcoal bed within the uncertainty of the measurements.

The high NO_x concentrations (>10 000 ppm) of the WCF process off-gas streams precluded the use of charcoal as a sampling medium. In these streams, a 55-g bed of silver zeolite beads was used as a collection medium. The sample was prefiltered before the silver zeolite bed with a high efficiency glass fiber filter (Gelman Type A/E). The flow rate was maintained at a nominal 32.5 L/min for sample periods from 3 minutes to 2 hours. The silver zeolite beds were transferred to 40-dram vials and counted on a LEPS in the same geometry as the charcoal beds. Although no collection efficiency studies were performed in situ, studies by Pence, et al.[19] show silver zeolite quantitatively retains both inorganic and organic forms of gaseous iodine under WCF off-gas conditions. Estimated absolute uncertainties associated with the use of the silver zeolite sample method are 20%. To date, the WCF sampling program has confirmed the results obtained at the ICPP stack.

3. WCF Mass Balance Results

The previously described analytical methodology was used to construct an ^{129}I mass balance to characterize the stack emissions more precisely and to determine the exact requirements of a continuous ^{129}I monitor. Data from two sample periods were used to perform the mass balance calculations. Some values used in the first sample period to obtain mass balance were averages of longer than two weeks. Therefore, these data were used only to confirm the values obtained in the second sample period when all samples were taken within a 12-hour period. Each sample period consisted of raw feed and scrub solutions sampled and analyzed in duplicate and off-gas samples taken at calciner stations 3, 4, and 5 and taken after the APS. A diagram of the WCF with the sampling points is shown in Figure 1.

Calciner sampling station 3 is located between the scrubber and the silica gel adsorbers, station 4 between the adsorbers and the HEPA filters, and station 5 between the filters and the APS. Additional sampling was not feasible due to the high personnel exposure that would be required. The APS combined off-gas sample station was not in operation during the first sample period. The assumption that the calciner was at steady state was made in order to compare the two sample periods.

The results of the two sampling periods are shown in Table V. The following conclusions were made:

1) The total removal efficiency of the silica gel adsorbers, HEPAs, and the APS for ^{129}I is less than 30%;
2) The low efficiency of the HEPAs and analysis of the sample prefilter indicate the emitted ^{129}I is predominantly gaseous;
3) Less than 31% of the ^{129}I charged to the calciner vessel as blended feed is emitted to the atmosphere; and 40-60% of the ^{129}I charged to the vessel is recycled in the scrub solution.

These results are not in agreement with studies performed by Wilhelm, et al.[20] at Karlsruhe. They found >99% of the ^{129}I was released during fuel dissolution. In addition, more than 74% of the ^{129}I was emitted as inorganic iodine. The preliminary tests at the ICPP indicate that less than 15% of the ^{129}I emitted was elemental. It is obvious, therefore, that the applicability of any ^{129}I monitoring system is inherently dependent upon the dissolution process chemistry. The development of the continuous ^{129}I monitor must be paralleled by an investigation of the waste solution chemistry of ^{129}I.

TABLE V

MASS BALANCE ANALYTICAL RESULTS

Process Stream	Sample Period 1 (nCi/sec)	Transmission Efficiency Period 1 (%)	Sample Period 2 (nCi/sec)	Transmission Efficiency Period 2 (%)
Raw Feed to Feed Mix Tank	29±3	NA	12±1	NA
Scrub Solution to Feed Mix Tank	43±4	NA	3.3 ± 0.3	NA
Calciner Vessel to Scrub via Off-Gas	68±7	94±20	6.9 ± 0.7	44
Scrub Tank to Adsorbers via Off-Gas	25±5	37±8	3.6 ± 0.7	52±10
Adsorbers to HEPAs	21±4	84±9	--	--
HEPAs to APS	21±4	98±9	2.75±0.54	--
APS to Stack	20±2	96±9	2.67±0.52	97±10

4. Other Gaseous ^{129}I Monitoring Methodology

The other methods of gaseous ^{129}I monitoring can be categorized into three types: oxidative dissolution[20], adsorption[21,22], and laser fluorescence[23]. Oxidative dissolution involves the scrubbing of the sample stream with an oxidizing solution (such as HNO_3) to oxidize all forms of iodine to soluble, non-volatile iodates. Of the oxidative dissolution methods, Horner's[21] electrolytic trapping of iodine from process gas streams would be appropriate for the collection of all forms of ^{129}I. A diagram of the apparatus is shown in Figure 4. This method removes the molecular, inorganic, and organic forms of iodine from process gas streams using the electrolytic oxidation of iodine in the presence of cobalt (III).

The gas stream is passed through the anode compartment of a partitioned electrolytic cell. A nitric acid analyte containing cobalt (III) oxidizes the effluent iodine to the soluble iodate species. The analyte is withdrawn and evaporated to dryness, leaving a residue of $Co(NO_3)_3$, $Co(IO_3)_3$, and $Co(IO_4)_3$ for analysis. This method gives high decontamination factors in the presence of NO_2 as shown in Figure 5. The advantages of this method include ease of operation and adaptability to fuel reprocessing plant off-gas streams. The primary disadvantages are: 1) additional treatment of the residue would be required before counting; 2) this pretreatment is not easily automated; therefore, its applicability to continuous ^{129}I monitoring is questionable.

The adsorption methods include the silver zeolite and charcoals previously described. A species selective iodine adsorber was evaluated by Emel, et al.[22] This sampler consists of three consecutive stages. The first stage is a bed of cadmium iodide which collects elemental iodide. The second stage contains 4-iodophenol, which quantitatively retains HOI. The third bed contains silver zeolite or triethylenediamine (TEDA)-impregnated charcoal. This third stage collects the organic iodides that penetrate the first two beds.

The primary advantage of this adsorption method lies in its ability to collect all forms of gaseous iodine while simultaneously differentiating the collected species. The primary disadvantage is that stack gas constituents, such as NO_x,[23] may alter the collection efficiencies. In addition, the conditions required for desorption are not well known and

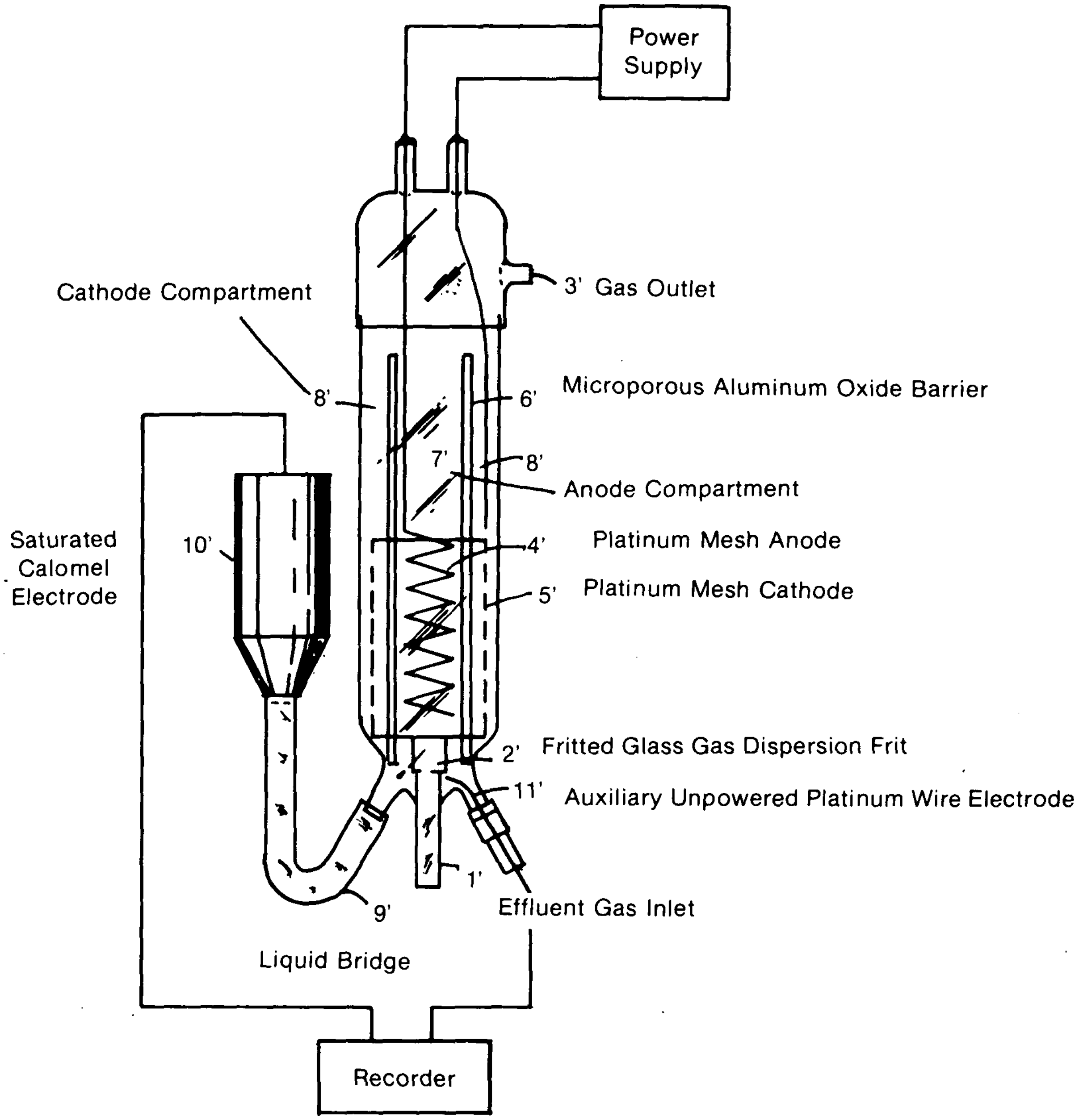

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Figure 4. Electrolytic Oxidizer

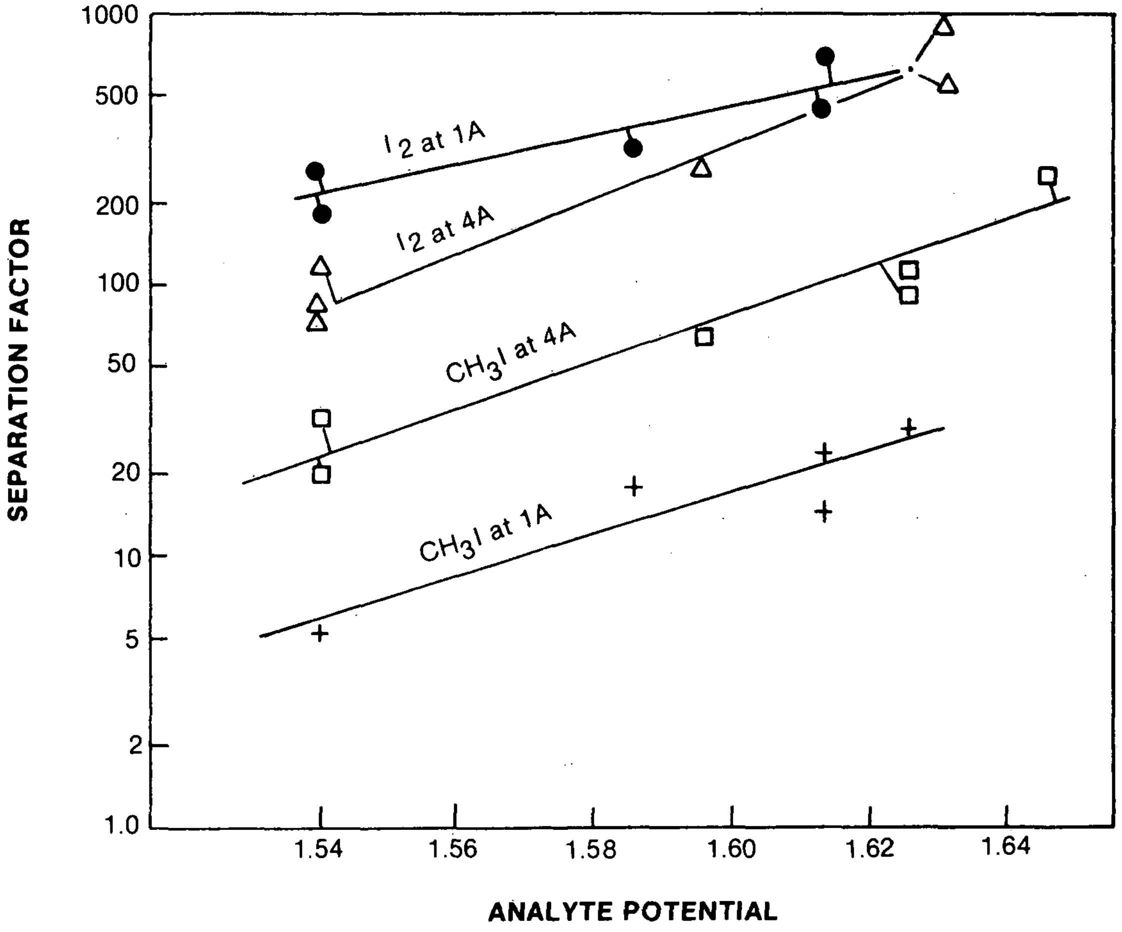

Figure 5. Separation Factor vs. Analyte Potential

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thus not easily automated for use in a continuous monitor. Therefore, adsorption methods may be used in the development to characterize the iodine emissions, but would not be of great use in a continuous iodine monitor.

The laser induced fluorescence method developed by Baronowski[23] is designed to be specific for elemental ^{129}I in ambient atmospheres. A catalytic converter transforms all organic iodides to the elemental form for detection. In this way, the detector serves as a total gaseous ^{129}I detector. The major disadvantage of this method is that the laser responds to NO_2. Therefore, some method of separating the ^{129}I from the NO_2 present in the sample stream is necessary. A method analogous to the permeation distillation method described in Section II is proposed. The iodine, after catalytic conversion to I_2, would be separated from NO_2 by permeation across thin membranes, followed by continuous detection by laser fluorescence. The integrated monitor is discussed in the following section.

V. INTEGRATED MONITOR AND DEVELOPMENT PLAN

The proposed integrated monitor is shown in Figure 6 . The catalytic oxidizer converts all organic forms of ^{14}C to $^{14}CO_2$. The permeation distillation device removes the $^{14}CO_2$ from the sample stream to be counted with an on-line proportional counter. Should higher than anticipated separation factors be found for the permeation distillation dryer, this proportional counter would be replaced with the more sensitive ionization chamber. The sample stream with the unsampled ^{129}I and ^{85}Kr is passed through a catalytic converter to form $^{129}I_2$, followed by a second permeation distillation device. The bulk partial pressures of the purge and sample streams are adjusted so that the $^{129}I_2$ is selectively removed from the interfering NO_x. The purge stream containing the $^{129}I_2$ may then be continuously monitored using laser fluorescence. The remaining ^{85}Kr in the sample stream would be monitored with a detector (surface barrier detector or $CaF_2(Eu)$) mounted in a flow chamber. The outputs of the three monitors are fed into a microprocessor which computes and prints release rates of ^{14}C, ^{129}I, and ^{85}Kr.

The development plan consists of the following tasks:

1) Evaluation of required conditions for quantitative catalytic conversion of ^{14}C to $^{14}CO_2$ and ^{129}I to $^{129}I_2$;

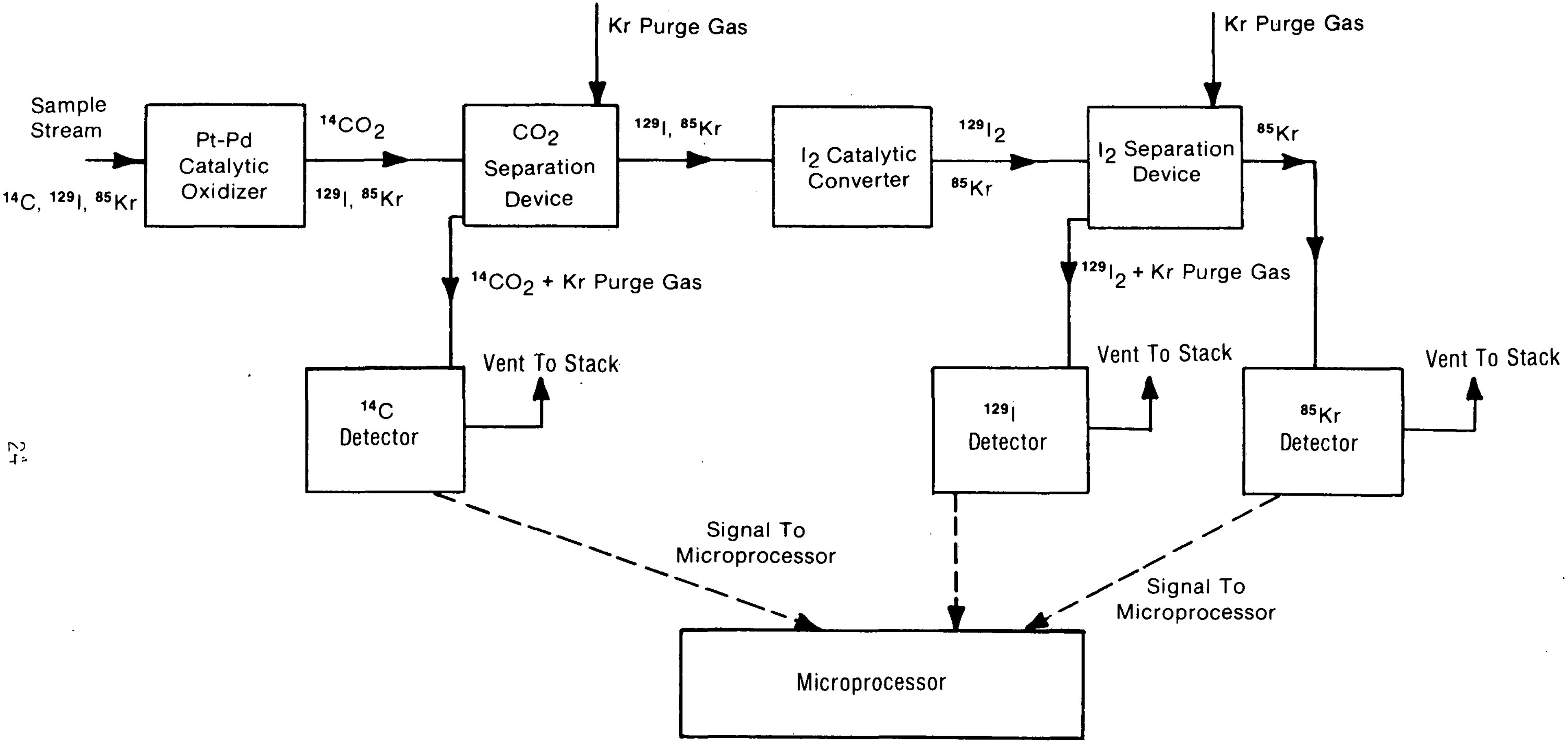

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Figure 6. **Integrated Monitor**

2) Determination of separation efficiency and chemical yield of the $^{14}CO_2$ and $^{129}I_2$ permeation devices;
3) Optimization and development of the detectors used for ^{14}C, ^{129}I, and ^{85}Kr;
4) Site testing of the integrated monitor during operation of all pertinent processes;
5) Parallel investigation of the ^{129}I waste chemistry to determine applicability of ^{129}I continuous monitor to other processes and plants.

VI. CONCLUSIONS

The state-of-the-art methods were evaluated for use in development of continuous ^{14}C, ^{129}I, and ^{85}Kr monitors. An integrated system was proposed to monitor each nuclide. The system consists of catalytic converters to oxidize ^{14}C to $^{14}CO_2$ and transform ^{129}I to $^{129}I_2$. The $^{14}CO_2$ and $^{129}I_2$ are separated from the sample stream using permeation distillation. The $^{14}CO_2$, once separated, is counted using either a flowthrough proportional counter or an ionization chamber. The $^{129}I_2$, once separated, is detected using laser fluorescence. The ^{85}Kr is monitored with a beta detector, either a surface barrier detector or a $CaF_2(Eu)$ scintillator, mounted in a flow chamber. The release rates are calculated with an on-site microprocessor. In addition, the liquid phase chemistry of ^{129}I in the process streams will be investigated in order to determine the applicability of the continuous iodine monitor to other reprocessing plants.

VII. APPENDIX

IODINE SEPARATION PROCEDURE

Approximately 10 mL of the feed sample is transferred to a 50-mL round-bottomed centrifuge tube containing 30 mL of distilled H_2O. One millilitre of KI carrier solution (10 mg/mL) is added, followed by 0.5 mL of 5% NaOCl. The mixture is allowed to react for 2-3 minutes.

Two millilitres of $1\underline{M}$ hydroxylamine hydrochloride are added to the tube, followed by 1 mL of $1\underline{M}$ $NaHSO_3$. Waste solutions are generally sufficiently acidic ($>2\underline{M}$ H^+) to make the final pH 1. A few drops of concentrated HNO_3 are sufficient to adjust the acidity if the pH is above 2.

Two millilitres of 2% $NaNO_2$ solution are added and the sample is mixed with 5 mL of toluene using a magnetic stir bar. Additional $NaNO_2$ solution is added if the organic phase is not deep red, indicating incomplete extraction of the iodine. After the aqueous phase is discarded, the organic phase is sufficiently decontaminated to be removed from the remote analytical facility. The remainder of the procedure may be carried out in a laboratory hood.

The toluene is transferred to a 250 mL separatory funnel. Ten millilitres of 1<u>M</u> $NaHSO_3$ are added to the toluene and the solutions are shaken until the organic phase is colorless. After discarding the toluene, add five drops of concentrated HNO_3, 10 mL of 1<u>M</u> $NaNO_2$, and 20 mL of toluene to the sample, and the iodine is re-extracted into the toluene. The iodine is back-extracted into $NaHSO_3$ and re-extracted into toluene twice more. A final back-extraction is made into 10.0 mL of 0.2<u>M</u> NaOH that contains 1 mL of 1<u>M</u> $NaHSO_3$. A 10% aliquot of this final solution is analyzed by potentiometric tritration with $AgNO_3$ to determine the chemical yield.

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