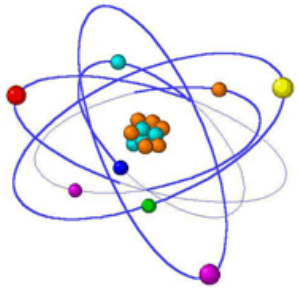
Radioisotope and Radiation Applications (FS2013)



Industrial Applications: Radiotracers (Week 5a, 2nd part)

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Radiotracer Applications: Outline

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Introduction

- Definition: Radiotracer techniques (RTT) comprise all methods in which **micro-amounts** (traces) of radionuclides or labeled compounds are added to a system, in order to pursue (trace) the fate, transport or chemical reaction of a certain element or compound in that system.
- Prerequisites of tracer application:
  - Tracers show the same behaviour as the atoms or compounds to be investigated (same chemistry for isotopes usually given, isotope effects can be taken into account (H/T)).
  - Labeling of elements or chemical compounds must be possible.
- Advantages:
  - Radionuclides can be measured accurately with **high sensitivity** at high dilution.
  - In some cases, RTTs offer information that cannot be obtained by other means.
  - Radiotracers are usually monitored external to the plant and so do not require shutdowns.
  - A wide variety of radionuclides and labeled compounds are commercially available.
  - Radiation safety: The radiotracer method, if all necessary precautions are taken, is safe.
  - RTT are complementary to numerical modeling approaches and can be used for benchmarking (validation of computational methods).

High Sensitivity

Number of atoms and mass of various radionuclides corresponding to 10 Bq.

Radionuclide	Half-life	Number of atoms	Mass [g]	Concentration if dissolved in 10 ml [mol/l]
^{238}U	$4.468 \cdot 10^{9}$ y	$2.0 \cdot 10^{18}$	$8.0 \cdot 10^{-4}$	$3.4 \cdot 10^{-4}$
^{226}Ra	1600 y	$7.3 \cdot 10^{11}$	$2.7 \cdot 10^{-10}$	$1.2 \cdot 10^{-10}$
^{227}Ac	21.77 y	$9.9 \cdot 10^{9}$	$3.7 \cdot 10^{-12}$	$1.6 \cdot 10^{-12}$
^{60}Co	5.272 y	$2.4 \cdot 10^{9}$	$2.4 \cdot 10^{-13}$	$4.0 \cdot 10^{-13}$
^{210}Po	138.38 d	$1.7 \cdot 10^{8}$	$6.0 \cdot 10^{-14}$	$2.9 \cdot 10^{-14}$
^{32}P	14.26 d	$1.8 \cdot 10^{7}$	$9.5 \cdot 10^{-16}$	$3.0 \cdot 10^{-15}$
^{24}Na	14.96 h	$7.7 \cdot 10^{5}$	$3.1 \cdot 10^{-17}$	$1.3 \cdot 10^{-16}$
^{251}Md	4.0 m	$3.5 \cdot 10^{3}$	$1.4 \cdot 10^{-18}$	$5.5 \cdot 10^{-19}$
^{258}Lr	3.9 s	$5.6 \cdot 10$	$2.4 \cdot 10^{-20}$	$0.9 \cdot 10^{-20}$

Detection limits of radionuclides (the amounts correspond to 1 Bq).

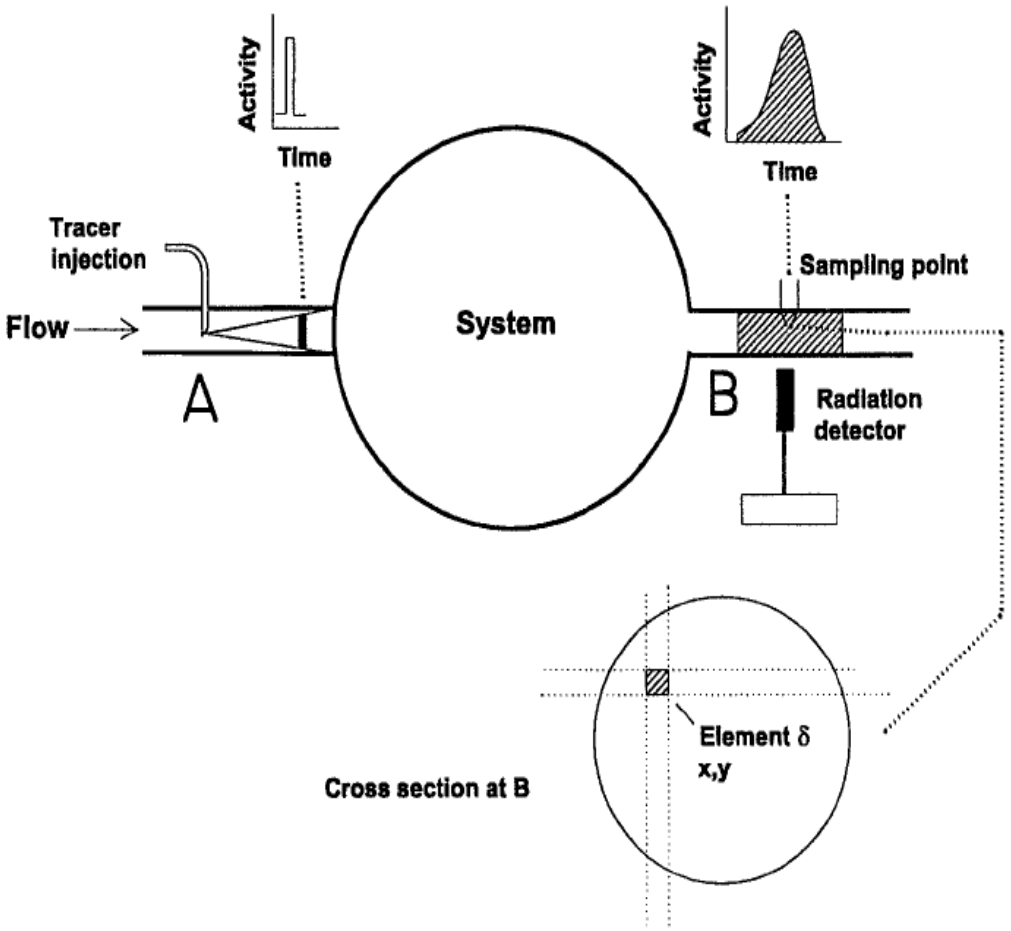
$t_{1/2}$	Detection limit Number of atoms N	mol
1 h	5 200	$8.64 \cdot 10^{-21}$
1 d	125 000	$2.08 \cdot 10^{-19}$
1 y	$4.55 \cdot 10^{7}$	$7.55 \cdot 10^{-17}$
10^{5} y	$4.55 \cdot 10^{12}$	$7.55 \cdot 10^{-12}$
10^{9} y	$4.55 \cdot 10^{16}$	$7.55 \cdot 10^{-8}$

- In principle, a single radioactive atom can be detected (if measured at the moment of its decay).
- Mass m and activity A of a radionuclide are correlated by the half-life $t_{½}$ (M=atomic mass):
  - $m = A\ M\ t_{½} / (\ln 2\ N_{Av})$
- Within 10 minutes and with an overall counting efficiency of 20% 10Bq can be detected with a statistical error of about 3%.
- Especially short-lived radionuclides can be measured with extremely high sensitivity (extremely low detection limits).
- Tritium can be determined in an atomic ratio down to **T:H ~ 10^{-19}**.

Fields of Applications

- Investigation of transport processes in industrial equipment.
- Study of corrosion and wear.
- Study of the kinetics of chemical reactions in equilibria (isotopic exchange reactions).
- Investigation of bonding and reaction mechanisms in (bio)chemistry.
- Measurement of diffusion and self-diffusion.
- Study of pathways of elements or compounds in biological systems, in the human body and in the environment.
- Radioanalysis.
- Application for diagnostic purposes in nuclear medicine.

General Concept



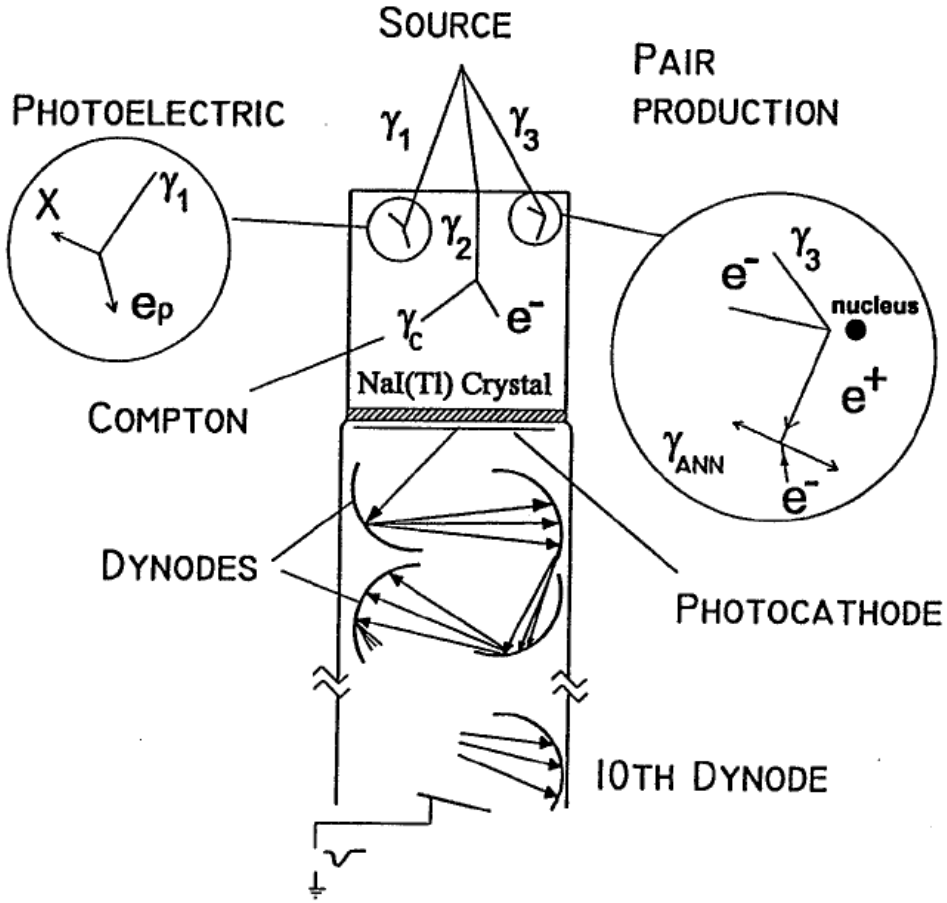
The principle of a tracer investigation. Radiotracers are used to track individual components of complex systems. A tracer is injected at A and its response monitored at B and interpreted in terms of the information sought on the behaviour of the system. The location of the radiation detector and the sampling point δ is shown.

- A small quantity (with no effect on the behaviour of the system) of a radiotracer (tracer population) is injected at point A, disperses through the system and is monitored at B.
- The concept of a 'system' should be interpreted in the broadest sense. (Theoretically: a system acts as an operator in mathematics.)
- The output (information) from such a system is either the counting rate from a strategically located detector or the radioactivity concentration of the tracer in fluid-samples.
- Complex tracer investigations possible:
  - various (radio)tracers may be used at the same time,
  - systems may be divided into subsystems,
  - other parameters of the system may also be monitored (correlations!),
  - interpretation often only with the aid of advanced computer modeling.

Choice of the Optimum Radiotracer / Examples

- The following (general) requirements have to be balanced:
  - The radiotracer should behave identically in essential respects to the component of the system which is under study.
    - chemical radioactive tracers are chemically identical with the traced substance
    - physical radioactive tracers merely fulfill a limited number of physical conditions
  - Consistent with the aims of the investigation, a shorter rather than a longer lived radionuclide should be chosen.
  - If practical, it is preferable to choose radionuclides emitting γ-rays in the range 150 to about 500 keV (less problems in handling and transport).
- Water tracing:
  - HTO (tritiated water) is used, although tritium (low-energy β particle emitter, E_{max}=18.6 keV) cannot be measured in situ.
  - For real time data the γ-ray emitters ^{82}Br, ^{131}I, ^{99m}Tc are used.
- For sediment and sand tracing it is necessary to match the particle size distributions and density of the natural material. Two methods are commonly used:
  - Samples are collected from the study area and made up as a slurry. A dissolved radioactive tracer such as ^{198}Au is added and adsorbs strongly to the surface (Used mainly for fine sediments).
  - Glass beads are synthesized with a particle size distribution and density matching that of the sand. The glass incorporates the required target material, which is irradiated in a reactor to form the tracer (^{140}La, ^{192}Ir, ^{110m}Ag).
- To study blast furnaces, the metallic tracers ^{198}Au, ^{60}Co are used to trace the iron, and ^{140}La to trace the slag.
- Isotope injections may be pulsed or at a constant rate over a longer time.

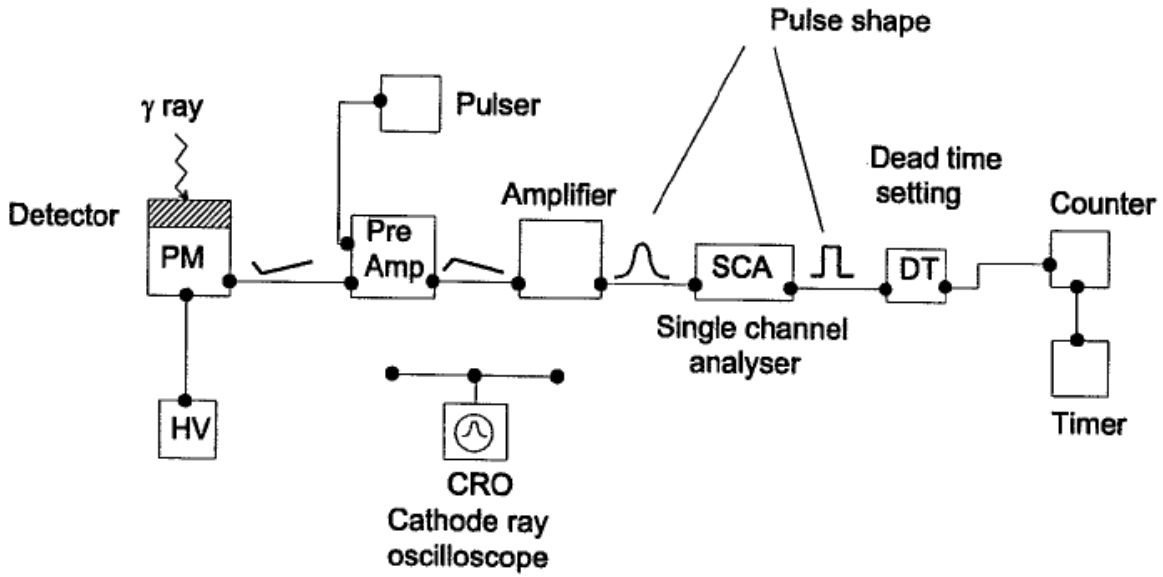
Tracer Detection



Gamma ray interactions in a NaI(Tl) detector shown with the associated electronics. The photoelectric effect (γ_1), Compton scatter (γ_2) and pair production (γ_3) are illustrated.

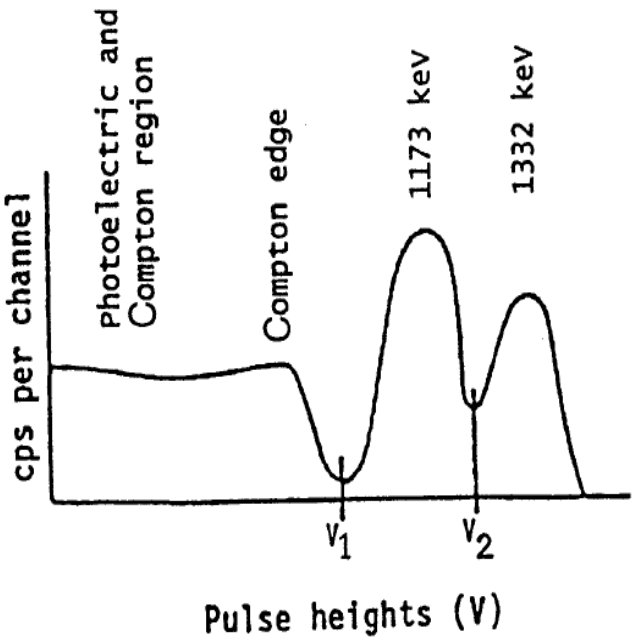
- Field monitoring systems comprise radiation detectors, ratemeters and either data loggers or output devices.
- Often **liquid scintillation detectors (NaI(Tl) crystals)** are used, because they are cheap, efficient and robust.
- Electronic equipment may be added (next slide).
- To enhance the detection efficiency integral counting can be used, i.e. the low-energy Compton scattered radiation is also measured.

Electronics in Counting



A block diagram of equipment used for the signal processing of pulses due to γ rays detected in a NaI(Tl) crystal (see text, Section 4.3.1 for explanations). The pulser and dead time gate (DT) are rarely required for routine work.

- Example: measured counting rate of the ^{60}Co γ-ray spectrum.
- Lower level (V_1) and upper level (V_2) discriminators may be used to select peaks (peak counting).



Micro-amounts of Radioactive Substances

- In radiotracer applications often micro-amounts (non-weighable amounts <1µg) of matter have to be handled, which requires special precautions.
- Terminology:
  - "Carrier-free" is used to indicate the absence of stable isotopes or longer-lived radioisotopes of the radionuclide considered (sometimes better: "no-carrier-added").
  - "Carrier-added" is used to indicate the addition of stable isotopes or longer-lived radioisotopes to the radioactive sample.
- Phenomena to be taken into account for micro-amounts (compared to macro-components):
  - Sorption on glass surfaces (ion-exchange capacity of ~10^{14} ions/cm^2, similar number of chemisorption sites).
  - Sorption of radionuclides on particulates in solution.
  - Radionuclides that are able to form crystals with the macro-component are incorporated at lattice sites:
    - in most cases the distribution is heterogeneous, i.e., the concentration varies with the depth
    - a heterogeneous distribution may even out over longer periods of time by diffusion or recrystallization
  - Coprecipitation of micro-amounts of radioactive substances by adsorption depends on the surface properties such as the surface charge and the specific surface area of the solid.
  - In ion-exchange and chromatographic procedures micro-amounts of radionuclides may be lost by sorption on the ion exchangers or sorbents or on the walls of the columns. Impurities in the materials used may be responsible for unexpected reactions and losses.
  - If the number of atoms or molecules becomes very small (<100), the usual thermodynamic descriptions are no longer applicable (single atom chemistry).
  - Radiocolloids (finely dispersed particles in a liquid phase, a gas phase or a solid) may be formed.

Application of Tracer Technology to Flow Studies

General Principles\Concepts

Investigation	Measurement	Mixing conditions
Dispersion	Dispersivities and/or dispersion coefficients	Not applicable
Flow rate measurements	Volume flow and/or mass flow	Complete mixing at the measurement cross section
Residence time studies	Residence time distribution (RTD)	Complete mixing at the inlet and the outlet of the vessel

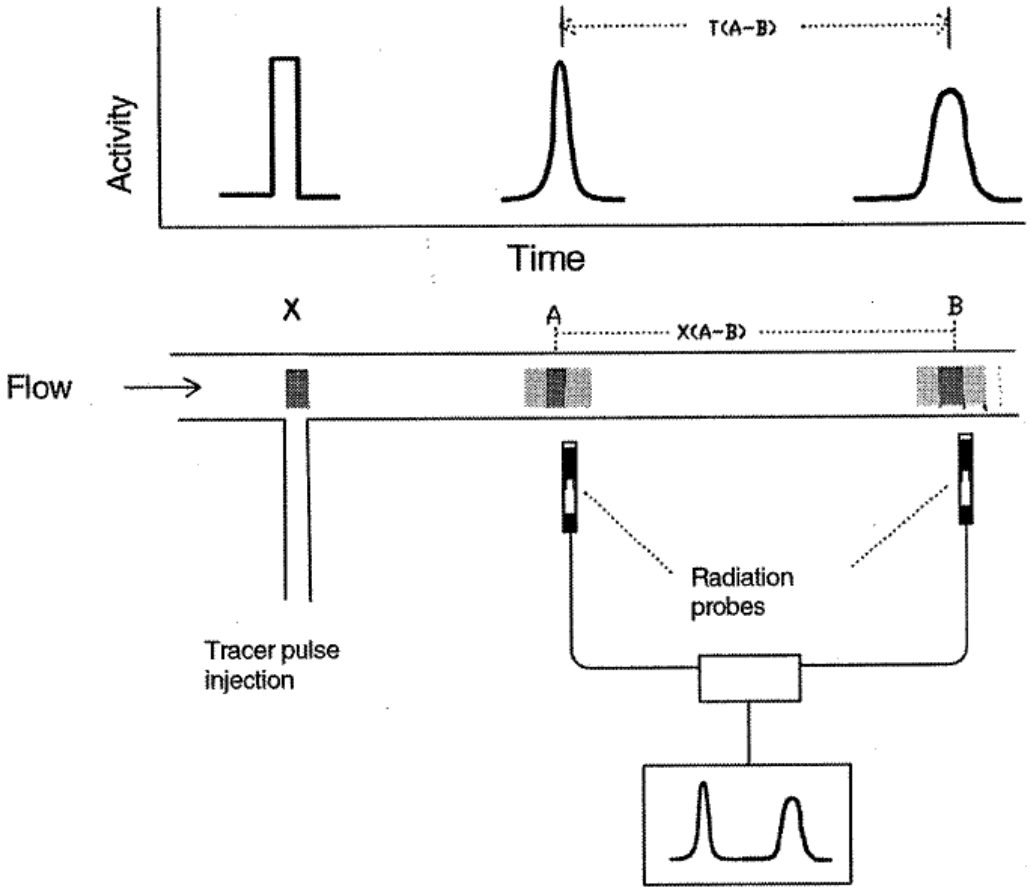
- Fluid Dynamics has been one of the most fruitful fields of radiotracer application.
- The investigations may be classified into the three classes shown in the table.
- Tracer dilution techniques can be used to determine flow rates provided **complete mixing (CM)** has been achieved:
  - For continuous injection at a constant rate CM is achieved when the radiotracer concentration is everywhere the same.
  - For pulse injections CM is achieved if the total amount of tracer removed during passage of the radioactive pulse is independent of the sampling point (element δ).
- **Residence or transit time (distribution)** of a fluid particle through a dynamic system (**RTD**). The counting rate response of the detector at B is a direct measure of the RTD of the tracer provided that:
  - the tracer is injected as an instantaneous pulse,
  - the bulk flow rate through the tank is constant.
- The **mean residence time (MRT)** is the average time taken by the tracer (and the fluid) to travel between the injection and measurement points.

Flow Rate Measurements: An Overview

- There are two fundamentally different approaches to measuring flow rate:
  - the pulse velocity method and
  - tracer dilution techniques
- The tracer dilution techniques may be subdivided according to the nature of the injection:
  - pulse injection
  - constant rate injection
- Furthermore, for pulse injection, two types of measurement may be distinguished:
  - total sample method
  - total count method

Flow Rate Measurements: Pulse Velocity Method

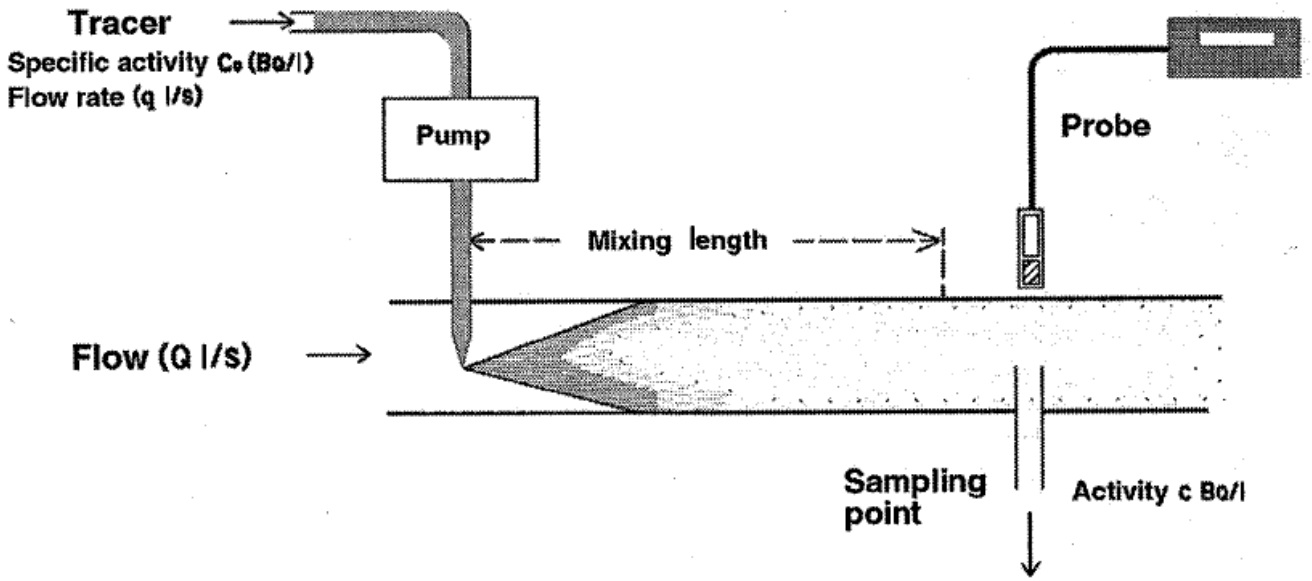
- Conceptually the simplest and most widely used technique.
- The average velocity of the pulse is given by:
  - $V_{A-B} = x_{A-B} / T_{A-B}$
- To calculate the volume flow Q_{A-B} from the linear velocity, the cross sectional area of the pipeline must be known.
- Extensively used for both liquid and gas velocity measurements.



Flow rate measurements: the pulse velocity or 'point to point' method. The tracer pulse is monitored at two locations following an instantaneous injection. Normally, the pulse maxima are adequate to define the interval T_{A-B}. For the most accurate work, the pulse profiles must be analysed.

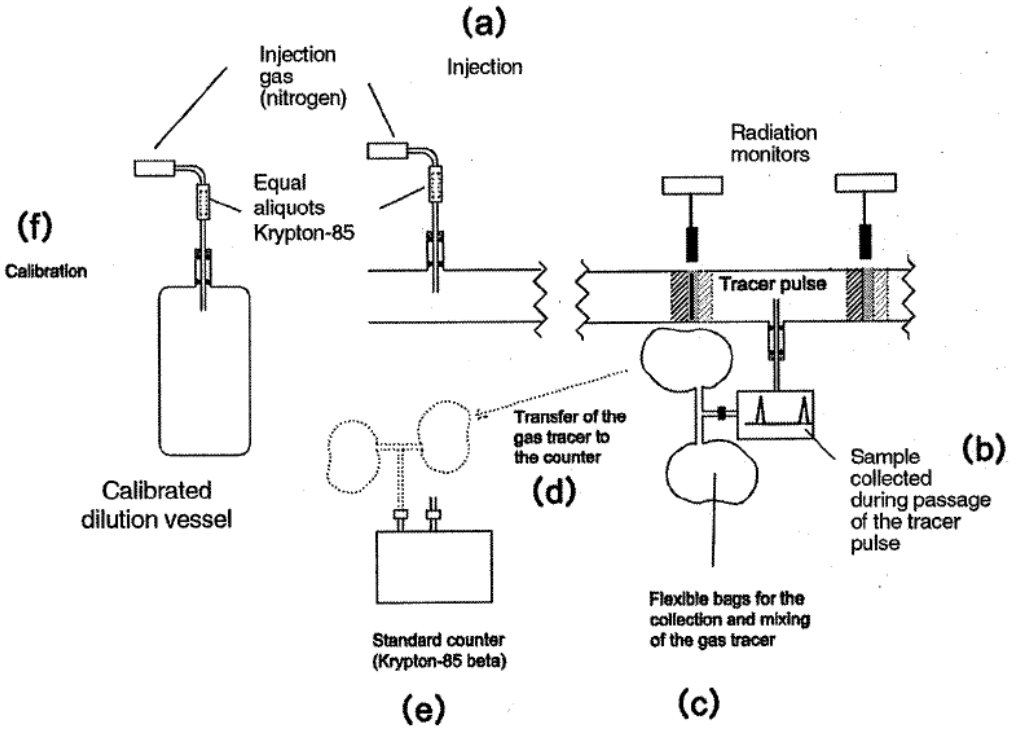
Tracer Dilution Method: Constant rate injection

- Volume flow rates may be calculated without knowledge of the cross sectional area (assuming CM).
- Due to mass/activity conservation of the tracer one has:
  - $qC_0=(Q+q)c$
- Thus the volume flow rate is given by (Q>>q):
  - $Q = qC_0/c$
- Experimentally, only the activity ratio C_0/c has to be measured.



Flow rate measurements: the continuous dilution method. The tracer is injected at a constant rate and monitored after complete mixing has been achieved.

Tracer Dilution Method: Pulse Injection/Total Sample Method



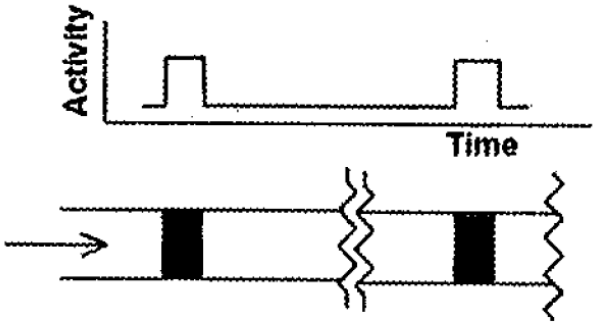
Gas flow using tracer dilution techniques. (a) Injection of an accurately monitored aliquot of ^{85}Kr as an instantaneous pulse using high-pressure nitrogen. (b) Collection of a sample of the gas containing the complete isotope pulse. This is achieved by locating radiation detectors upstream and downstream of the sampling point and monitoring the ^{85}Kr gamma emission. (c) The sample inflates the flexible bags and is well mixed. (d), (e) The sample is transferred to the standard counter and the activity registered. (f) A second aliquot is added to a calibration vessel, mixed and transferred to the standard counter.

- As an example, a gas flow rate measurement is illustrated in the figure.
- Assuming CM at B, the total flow rate Q [liter/s] is given by (A=activity of tracer, q=sampling rate [liter/s], a=tracer activity in the sample):
  - $Q = qA/a$
- Only the activity ratio A/a has to be measured.
- Effective sampling rate q is (v=volume of the gas in the counting chamber, ΔT=sampling time):
  - $q = v/\Delta T$
- Better accuracy when a calibration vessel is used ($A/a_c = V/v$):
  - $Q = (a_c/a)\,(V/\Delta T)$

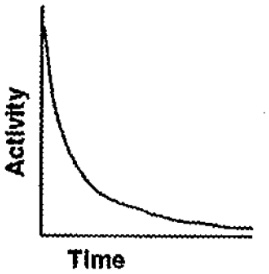
Tracer Dilution Method: Pulse Injection/Total Count Method

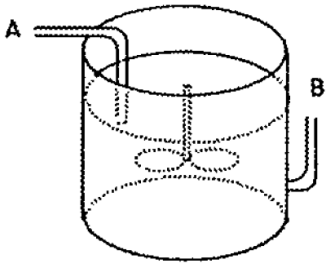
- Essential feature: The flow rate is determined from the cumulative response of a strategically located detector (immersed in the liquid or located externally).
- The total # of counts N (corrected for background and decay) is registered and the flow rate Q [liter/s] is given by (A [Bq] = total injected activity, F [cps per Bq/l] = calibration factor relating A to N):
  - $Q = AF / N$
- The calibration factor F must have been determined before:
  - The calibration of fully immersed detectors involves recording their responses [cps] to known tracer concentrations [Bq/l] in a large tank.
  - For the calibration of detectors placed external to pipelines a section of similar pipeline must be set up, and the response of a similarly located detector to a known activity within the pipe must be measured.

Residence Time Distribution (RTD)



(a) Plug flow

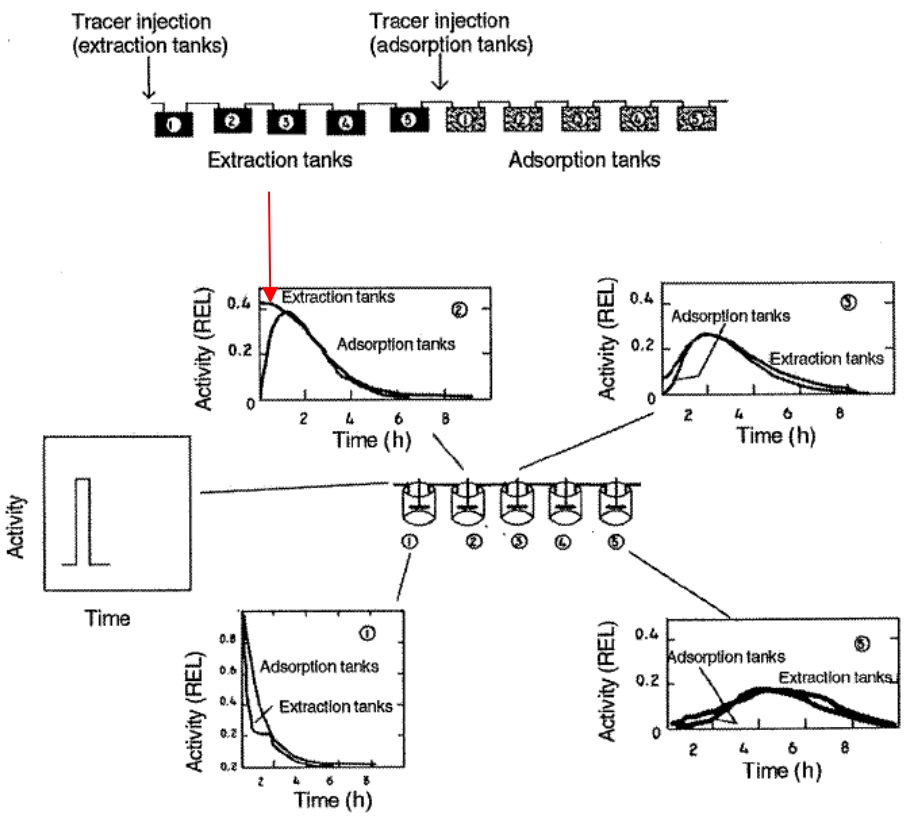




(b) Stirred flow

- The efficiency of many industrial processes depends on ensuring optimum contact between the various reactants or between reactants and catalysts, e.g.:
  - catalytic conversions in the chemical and oil refining industries,
  - leaching processes in the minerals extraction industry,
  - aeration of dispersed sewage in inland disposal ponds.
- Radiotracer techniques have been widely used to assess both the mixing processes and the RTDs of the reagents.
- Mixing and transport are invariably complex. The experimental procedures can be illustrated using ‘plug flow’ and ‘stirred flow’ approximations.
- (Idealized) plug flow: completely regular, steady flow:
  - MRT = V / Q (V=volume, Q=mean flow rate)
  - E.g.: The below design performance of a sewage pond could be analysed using the tracers HTO and ^{99m}Tc.

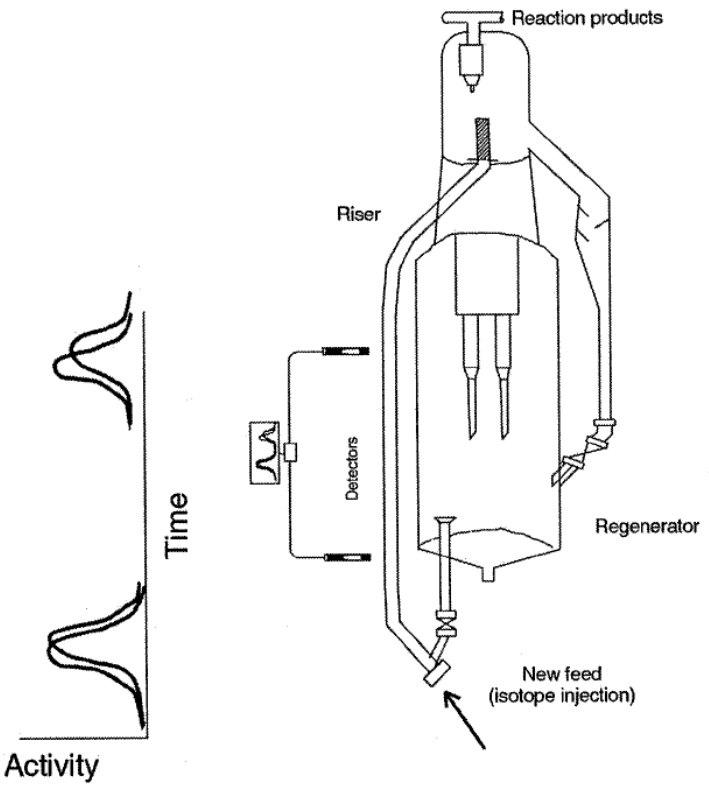
Residence Time Distribution: Stirred Flow



RTD study in the gold extraction industry. A sequence of five extraction tanks and five adsorption tanks in series. An instantaneous pulse of tritium is injected at the inlet to the first extraction and to the first adsorption tank. The tritium concentrations after the first, the second, the third and the fifth tanks are shown graphically as a function of sampling times. The profiles in tank 4 may be inferred from those in 3 and 5. The extraction and adsorption tanks show significantly different behaviour.

- (Idealized) stirred flow: an injected pulse of tracer is instantaneously dispersed uniformly through the liquid in the tank and leads to an initial concentration of $C_0 = A / V$.
- The figure shows an example from the gold extraction industry:
  - Yield in the plant was lower than expected.
  - In the first five tanks gold is leached from the crushed ore with a solution of sodium cyanide (0.02 to 0.05% NaCN).
  - In the second sequence of tanks the gold precipitates onto a slurry of charcoal.
  - Tritium was used to trace the aqueous phase, separately for both series of tanks.
  - Short circuiting was found at the outlet of the second leaching tank (red arrow).
- In practice flow patterns are very complex; computer fluid dynamics (CFD) codes are applied for holistic modeling of flow patterns.

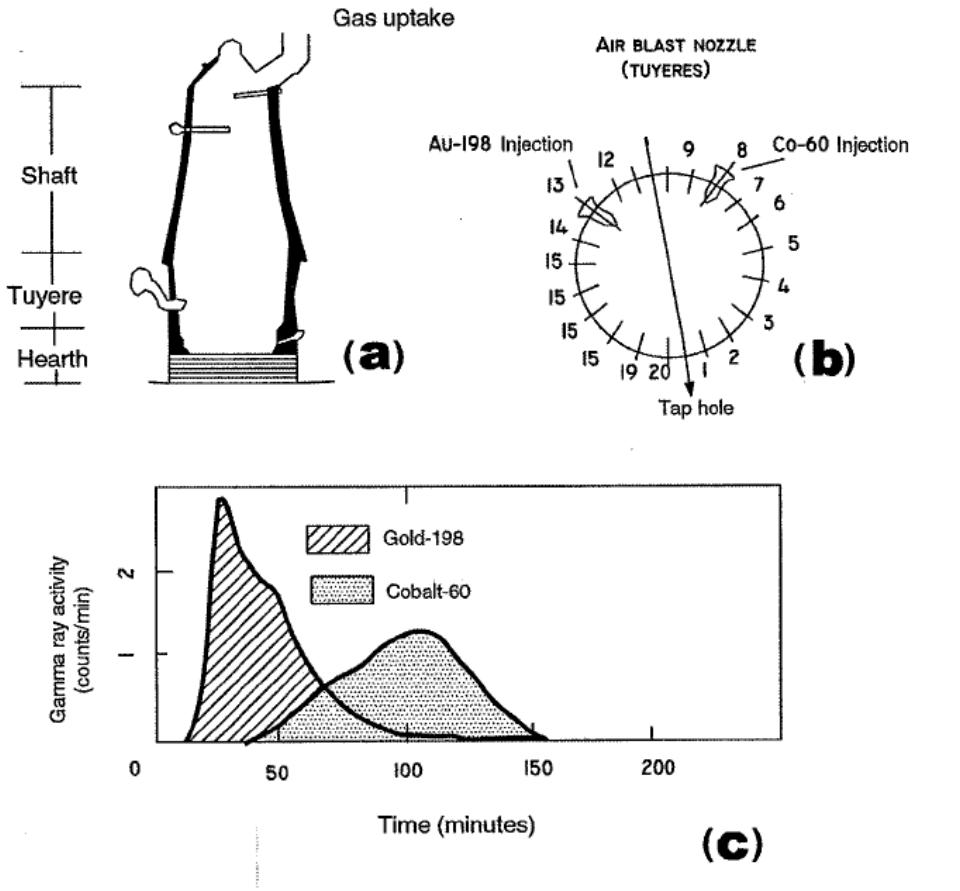
Case Studies: Fluidized Catalytic Cracking Unit (FCCU)



A schematic representation of an FCCU illustrating the investigation of the dynamics of the gas phase and the catalyst in the riser.

- Catalytic cracking: the production of gasoline range hydrocarbons from the higher boiling fractions of crude oil.
- FCC is central to the operation of modern petroleum gasoline refineries (US: amount of feed processed by FCCUs was ~35% in 1991).
- FCCUs should operate at peak performance. Investigations are complex, because there are 4 major process streams: fresh feed, catalyst, steam and air.
- Radiotracers offer a uniquely powerful approach for studies, because:
  - different process streams can be separately labeled and independently monitored (e.g., ^{85}Kr is used to trace the gas phase, the catalyst is activated in a reactor)
  - externally placed detectors do not interfere with production schedules
  - FCCUs are too complex to enable sufficiently precise diagnostics using mathematical models alone
- A radiotracer injected into the riser can be used to provide information on:
  - feed and catalyst distribution in the riser feed zone
  - catalyst and vapour velocities in the riser
  - determination of efficiency of the riser termination device
  - RTDs through the reactor and stripper
  - mixing and flow characteristics in the reactor and stripper
  - cyclone efficiencies, flow distribution and residence times

Case Studies: Blast Furnace Efficiency



Radioisotope study: blast furnace efficiency. (a) Schematic representation of a blast furnace showing an air blast nozzle (tuyere) and a tap hole. (b) The location of the tuyeres, the tap hole and the isotope injection points. (c) The variation with time of the activity of cobalt-60 and gold-198 in the iron sampled from the tap hole (after Easey, 1988).

- Blast furnaces are used to reduce iron ore to iron using coke to which is added a flux such as limestone or quartzite. Basic reaction:
  - $Fe_2O_3 + 3\ CO \rightarrow 2Fe + 3CO_2$
- The performance of the furnace depends on many factors:
  - quality of the coke
  - uniform mixing of CO gas with the iron
  - efficiency of the hearth drainage
- Investigation of reduced yield by injection of two radiotracers, ^{198}Au and ^{60}Co through two **symmetrically located** air blast nozzles.
- During the tapping process samples were taken. The differing response curves for ^{198}Au, ^{60}Co indicate that the reduced yield was due to development of cold spots within the hearth.

Case Studies: Determination of Inventories

- Principle: A small accurately known quantity of tracer of specific activity A_0 is injected into the bulk, and, after CM, the (much lower) specific activity ã of the material is measured. The basic equation is (M=mass of total inventory, m=mass of the added radiotracer): $\mathbf{M = mA_0/ã}$
- The activity ratio A_0/ã must be measured with high accuracy. To this end often the dilution method is used (k_D=dilution factor, $ã_0$=specific activity of the tracer after dilution): $\mathbf{A_0 = k_D \cdot ã_0}$
  - Then the total mass is given by: $\mathbf{M = m\, k_D\, ã_0 / ã}$
- Example: Measurement of mercury (Hg) in industrial plants designed for production of chlorine and sodium hydroxide (HOCl, NaOH) by the electrolysis of sodium chloride (NaCl) solutions.
  - The Hg (used for electrodes) inventory must be carefully monitored for environmental reasons.
  - Radioactive mercury (mainly ^{197}Hg, ^{203}Hg) is produced in a reactor by irradiation of stable mercury.
  - The radioactive mercury (mass m, activity A_0) is added to the large reservoir, and, after CM, ã is measured to calculate the mass M of the reservoir.
  - Which radionuclide is used is determined by the time required to achieve homogeneous mixing. (The half lives of ^{197}Hg and ^{203}Hg are 64.1h and 46.6d, respectively.)
  - Measurement accuracy better than 1% can be achieved routinely.

Summary (1): Applications of artificial tracers to industry

Industry sector	Investigation	Applications
Refining	Fluidised catalytic cracking units (FCCUs)	Velocities of vapour and the catalyst in the riser; separation efficiency of the catalyst and vapour
	Leakage and blockages in pipelines and chemical reactors	* Short circuiting through catalyst * leakage and blockages in sub-surface pipelines
	Fluid flow rates	* Meter calibration – liquid and gas flow * Mass balance studies
Oil and gas field	Effectiveness of enhanced oil recovery strategies based on injection of water (with additives) or gas into the field at selected locations	* Used to identify, for example, short circuiting; * Validation of mathematical models of the process
	Leakage between gas bearing strata in a production field	^{85}Kr or T (or ^{14}C) labelled light hydro-carbons injected at observation wells and migrate to production wells
Chemical	Flow rate measurements for *in situ* meter calibration	Point to point and tracer dilution methods widely used
	Mercury inventories	Tracer dilution using ^{203}Hg and/or ^{197}Hg
	Leakages and blockages	
Minerals	Process optimisation	Frequently involve (RTD) studies
	Hot processing of ores and concentrates	Wide range of tracer techniques to study the processes in blast furnaces and roasting furnaces
	Electrorefining	Measuring the efficiency of the electrolytic production of Al
Iron and steel	Blast furnaces	Refractory lining wear. Sealed ^{60}Co sources into selected refactory bricks during lining – as bricks erode pellet also erodes and radiation level falls
	Blast furnaces	Simultaneous RTD studies on the iron and slag
Cement	Pre-mixing silos	Efficiency of mixing of the four components, stock in silos
	Rotary kiln	Residence time studies
Mechanical engineering	Wear tests	Activation of pistons or cylinders and monitoring of activity of eroded material in test rig

Summary (2)

- Radiotracer techniques have been extensively used throughout industry since the mid-1950 to:
  - obtain an improved understanding of industrial processes
  - diagnose the reasons for industrial plant operating below specification
  - obtain accurate measurements of flow rates, inventories and mixing efficiencies
- The evolution of radiotracer technologies has been influenced by enormous developments in microprocessor technology, data processing and visualization.
- Radioisotope applications are highly regulated (radiation safety), which complicates their employment.
- Techniques developed for the health sciences are being applied to industry (e.g. computerized tomographic imaging).
- Goal for the future: Maximize the amount of information obtained with radiotracers with a minimum use of radioactivity (ALARA principle).
- Tracers are now seldom used in isolation, but in conjunction with a range of investigation techniques.

Literature

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  Chapter 8

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