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A Specialist Periodical Report

Radiochemistry

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A Review of the Literature Published during 1974
and 1975

Senior Reporter

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Foreword

The general design of this volume is different from the previous two in that it is concerned entirely with some of the applications of radioisotopes, one chapter being devoted to industrial uses, one chapter to archaeology, and two chapters to some utilizations of medical importance. It has been the intention to give a comprehensive cover of the literature from 1973 to late 1975 or early 1976, and the Reporters apologize for any significant omissions or misrepresentation.

G.W.A.N.

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By J. A. Heslop

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Industrial Applications of Radioisotopes

BY J. A. HESLOP

The application of radioisotopes to the study of industrial process and to the measurement and control of those processes is well established. This review will contain little that is radically novel in terms of basic techniques or applications. There exists, however, a basic information gap between the radioisotope applications specialist and the user, be he chemical engineer, R and D scientist, or civil engineer. This gap causes the use of radioisotopes as tracers or in instruments to be considered as a last-gasp effort that is to be used only when all else fails. Experience has shown that the use of radioisotopes can often solve problems much more easily than conventional techniques, and, in cases where the radioisotope specialists are part of the industry or belong to an institute with good industrial contacts, the number of radioisotope applications can show an amazing growth (e.g. the group at ICI Petrochemicals Division who are concerned with the application of radioisotopes within industry complete well in excess of 1000 applications per year). It is hoped that this review will help to bridge the information gap in that it covers recent applications of radioisotopes in industry up to about mid-1975.

The field has already been the subject of a number of general reviews which cover the basic principles and certain applications.¹⁻⁴ Specific reviews covering applications in the textile and fibres industry,⁵⁻¹⁰ in plastics,¹¹⁻¹³ and in the basic metals industry¹⁴ have been published.

1 Radiotracers¹⁵

It has been said that there is no such thing as the perfect tracer, as this material

¹ E. W. Stene, J. H. B. George, and H. P. Beutner, Isotopes in Industry Contract AT (30-1)-3337, United States Atomic Energy Commission.

² L. J. Taylor, *Reports Progr. Appl. Chem.*, No. 19, p. 673.

³ H. Simpson, *Reports Progr. Appl. Chem.*, No. 19, p. 243.

⁴ J. S. Charlton, J. A. Heslop, and P. Johnson, *Physics in Technol.*, 1975, 67.

⁵ W. Markiewicz, *Przegląd Włokienniczy*, 1973, 27, 299.

⁶ J. Luenenschloss, (Eurisotop-77) Commission of the European Communities, Brussels, 1973.

⁷ H. Beckstein, *Chemiefasern Text-Anwendungstech./Text. Ind.*, 1973, 23, 36.

⁸ R. Merkle, *Izotopotechnika*, 1973, 16, 593.

⁹ R. Merkle, *Chem.-Anlagen Verfahren*, 1973, 164, 71.

¹⁰ V. S. Akopov, N. Yu. Myrin, and V. I. Postnikov, 'Methods for the Technical Economies: Analysis of the use of Radioisotopic Control Methods in Industry', Atomizdat, Moscow, 1974.

¹¹ A. Kosmowski, *Konstr. Elem. Methods*, 1973, No. 4, p. 113.

¹² L. Trajkov, *Khim. Ind. (Sofia)*, 1972, 44, No. 5, p. 220.

¹³ B. Ya. Munkov, *Trudy Vses. Nauch.-Issled. Inst. Gidrotekh. Melior*, 1970, 48, 8.

¹⁴ 'Nuclear Techniques in the Basic Metal Industries,' Proceedings of Symposium at Helsinki, July 1972, IAEA, Vienna, 1973.

¹⁵ C. W. Sheppard, 'Basic Principles of the Tracer Method', Wiley, New York, 1962.

would be indistinguishable from the population as a whole. Isotopes usually provide the nearest approach to the perfect tracer, in that they are, to a good first approximation, chemically and physically indistinguishable from the total population. If they are also radioactive then they possess a useful property (the emission of radiation) which can be related to their concentration in the bulk of the medium under investigation. There are several degrees of sophistication possible in the selection of a tracer. If the medium under investigation undergoes a chemical reaction or a phase change, then a tracer which parallels this behaviour must be selected, and hence the chemical form of the tracer must be identical with the bulk material. If this criterion can be satisfied, then, neglecting any possible isotope effects, the ideal tracer will be used.

In the chemical industry, the isotopes which come into this category are usually ^{14}C and ^3H , both of which can be readily incorporated into organic materials. These isotopes are far from ideal for use in industry, in that they are both weak β -emitters and hence cannot easily be detected inside process equipment, and sampling is necessary. They both have long half-lives and hence cannot easily be used to study problems in which they would end up in a product which would be sold to the general public. Despite these disadvantages, there are certain problems which can only be solved by the use of ^{14}C or ^3H , and, provided the financial incentive is large enough, both isotopes can be used on full-scale plant both efficiently and safely. On smaller scale equipment and in the laboratory ^{14}C and ^3H play very important parts in industrial monitoring.

In a majority of situations, where the bulk property of a material is being followed, there are no physical or chemical changes, and it is possible to use a physical tracer. This type of tracer will follow the bulk movement of a material, provided that it does not undergo a phase change or a chemical reaction. Similarly, the tracer itself must not be precipitated or in any way lost from the material being traced. It is often sufficient if the material is simply soluble in the medium, as in the use of $\text{NH}_4^{82}\text{Br}$ for the tracing of aqueous streams. The use of a physical tracer allows a γ -radiation detector to be used outside the process vessel, and hence removes the need for samples to be taken. This means that short-lived isotopes can be used, thus reducing the problems of radiological protection. Table 1¹⁶⁻²⁷ is a list of a number of isotopes which have been used in the study of various industrial problems. The isotopes are in general produced in a nuclear reactor and are of sufficiently long half-life to allow easy transport to the industrial site. Exceptions to this are ^{41}A and ^{56}Mn , whose half-life requires reasonably rapid access to an isotope production facility. The production of isotope generators for use in medicine has not been widely applied in industry, usually because the γ -energy requirements are different, although

¹⁶ M. Brown, *Internat. J. Applied Radiation Isotopes*, 1974, **25**, 289.

¹⁷ H. H. Gomez, O. Cuello, and S. Rey, *Nuclear Sci. Abs.*, 1974, **29**, 18 546.

¹⁸ E. Garcia Agudo, U. Dante, T. Ohara, and W. Sanchez, *Nuclear Sci. Abs.*, 1975, **31**, 664.

¹⁹ K. Runge and G. Grahl, *Isotopenpraxis*, 1974, **10**, 133.

²⁰ L. Riedlmayer, J. Riesing, and V. Muehldorf, *Nuclear Sci. Abs.*, 1975, **31**, 14 259.

²¹ J. L. Boutaine, Boeing-747 Specialists Meeting, Everett, Washington, U.S.A., February 1974.

²² B. A. Fries, (Chevron Research Co.) U.S.P. 3 809 898, 7 May 1974.

²³ W. J. McCabe, K. P. Pohl, and O. J. Rowse, *Nuclear Sci. Abs.*, 1975, **31**, 14 257.

²⁴ K. Krishnamurthy and S. M. Rao, *J. Hydrol.*, 1973, **19**, 189.

²⁵ Y. S. Kim and B. H. Lee, *J. Korean Nuclear Soc.*, 1974, **6**, 231.

²⁶ J. Lontiadis and C. Dimitroulas, *Nuclear Sci. Abs.*, 1974, **29**, 24 206.

²⁷ B. Gorski, C. Beyer, and H. Ulrich, *Isotopenpraxis*, 1973, **9**, 282.

Table 1 Radiotracers for process studies

Isotope	Half-life	Emission used	Chemical form	Medium
⁵⁶ Mn	2.6 h	γ	Acetate ⁴	Aqueous
			Naphthenate ⁴	Organic
²⁴ Na	15 h	γ	Carbonate ^{4, 16, 17}	Aqueous
			Naphthenate ⁴	Organic
			Salicylate ⁴	Organic
⁸² Br	36 h	γ(var 0.55–1.48 MeV)	Ammonium bromide ^{4, 18}	Aqueous
			KBr ⁴	Aqueous
			<i>p</i> -dibromobenzene ⁴	Organic
			Methyl bromide ⁴	Gas
			Ethylene dibromide ²⁰	Gas/liquid
¹⁴⁰ La	40 h	γ	Oxide ^{4, 17}	Solid
			Acetate ^{4, 19}	Aqueous
			Naphthenate ⁴	Organic
¹⁹⁸ Au	2.7 d	γ	Colloidal ⁴	Organic
¹²² Sb	2.8 d	γ	Sb ₂ O ₃ ⁴	Solid
⁴¹ A	110 min	γ(1.29 MeV)	Element ^{4, 16}	Gas
¹²⁵ Xe	18 h	γ	Element ⁴	Gas
¹³³ Xe	5.3 d	γ(81 keV)	Element ^{4, 21}	Gas
⁸⁵ Kr	10.6 y	γ(0.51 MeV)	Element ^{22, 23}	Gas
⁴⁶ Sc	84 d	γ	Glass ²⁴	Solid
¹⁹² Ir	74 d	γ	Glass ²⁴	Solid
⁵¹ Cr	27.8 d	γ	edta complex ^{25, 26}	Aqueous
³ H	12 y	β	} Depends on chemical form of system under investigation ²⁷	
¹⁴ C	5.7 × 10 ³ y	β		

a ¹⁴⁰Ba/¹⁴⁰La generator has been successfully developed and used by Runge and Grahl¹⁹ to investigate matter-transport processes in chemical plants.

Flow Measurements.³¹—Most industrial processes require measurements of mass flow in order that the efficiency of their operations can be monitored. A large number of conventional flowmeters exist but they often need calibration, or the measurement of an unmetered flow is required. Radioisotope methods have achieved a wide acceptance, often as standard methods of flow measurements where high accuracy is required, for example in the measurement of a mass balance on a plant.

There are several radiotracer methods of flow measurement in common use. The simplest is the pulse-velocity measurement, in which a sharp pulse of radioactivity is injected into the stream whose flow is to be measured. The passage of the pulse is observed by a pair of detectors positioned downstream of the injection pipe at a distance such that lateral mixing within the pipe is complete. The flow rate is given by $Q = lA/t$, where Q is the volume flow rate, A the cross-sectional area, l is the distance between the two detectors and t is the time taken for the radioactivity to travel the distance l . If a γ -emitting isotope is used then the detectors can be outside the pipe and can be connected to either simple or integrating ratemeters. In both cases the time t is obtained by measuring the time interval between the peak half-height positions. The method requires turbulent flow in the pipe and a knowledge of the internal pipe diameter, which must be effectively constant. This latter measurement can be obtained by measuring the external diameter of the pipe and then the

pipe wall thickness, using, for example, an ultrasonic method. If accurate flow rates are required this is done at several points along the pipe length, and measurements are also made of the pressure (for gases) and temperature within the pipe.

Under ideal conditions, Evans *et al.*²⁸ measured the flow rate of air along a pipe, using ^{85}Kr at flow rates varying from 3 to 300 l s^{-1} . Over 90% of a total of 61 tests carried out had a mean deviation of $< \pm 0.4\%$ from the flow rate determined by collection of the gas over a given time interval.

Under industrial conditions it is difficult to achieve this sort of accuracy, but deviations of ± 1 – 2% are usually easily achievable, and under conditions in which the pulse-velocity technique can be used it will be the method of choice for flow measurement.

Flows of liquids and gases can also be measured by a dilution technique in which a radioactive tracer (radioactive concentration S_1) is continuously injected at a rate q into the material flow. Samples are taken at a suitable distance from the injection point. If S_2 is the radioactive concentration at the sample point and Q is the flow rate to be measured, then

$$qS_1 = (Q + q) S_2 \quad (1)$$

$$Q = q(S_1 - S_2)/S_2 \quad (2)$$

In general, $S_1 \gg S_2$.

$$Q \approx q S_1/S_2 \quad (3)$$

Provided that turbulent flow exists, the measurement of flow rate is independent of the vessel diameter and any changes in it, and hence the method can be used in situations where the pulse-velocity-method cannot be applied. Injection is continued until a radioactivity 'plateau' is obtained at the sampling point, and this can be measured with good precision. The radioactive concentration of the injected material and the rate of injection can be accurately measured, and hence overall accuracies of $\pm 1\%$ can be attained.

The accuracy of the method has been tested against direct weighing by measuring the flow rate along a pipe to a road tanker by the dilution method and comparing this with the weight of material found in the tanker. The results²⁹ shown in Table 2 show the excellent agreement obtained between the direct method and the dilution technique. This method has been applied by Clayton and Evans³⁰ to the measurement of flow through turbines and pumps in power stations and is in routine use throughout ICI for the measurement of a wide variety of gas and liquid flow rates. Gas flow rates in excess of $10^5\text{ m}^3\text{ h}^{-1}$ and liquid flow rates greater than 10^6 gallon h^{-1} have been measured.

A third method of flow measurement exists which is useful for the measurement of large flows in open channels.³¹ The dilution sudden-injection method has a number of variations but essentially consists of the injection of a suitable tracer for a short duration, followed by downstream sampling over a period of time sufficiently long to ensure that the whole of the tracer has passed the sampling point.

²⁸ G. V. Evans, R. Spackman, M. A. J. Aston, and C. G. Clayton, in 'Modern Developments in Flow Measurement', ed C. G. Clayton, Peter Peregrinus Ltd., London, 1972, p. 245.

²⁹ P. Johnson and J. Whiston, unpublished work.

³⁰ C. G. Clayton and G. V. Evans, in ref. 28, p. 276.

³¹ International Standard; Ref. No. ISO 555/11-1974 (E).

Table 2 Measurement of liquid flow by the radioisotope dilution method. A test of the accuracy of the method compared with direct weighing.²⁹

Sample time/min	Radioactive concentration/ counts s ⁻¹ ml ⁻¹	Instantaneous flow rate/ton min ⁻¹
2	0.330	0.355
4	0.331	0.354
6	0.331	0.354
8	0.334	0.351
10	0.336	0.350
12	0.335	0.350
14	0.335	0.350
16	0.337	0.348
18	0.338	0.348
20	0.337	0.349
22	0.341	0.344
24	0.340	0.345

Radioactive concentration of injection solution = 6.93×10^4 counts s⁻¹ ml⁻¹; rate of injection = 19.74 ml min⁻¹; time of addition = 24 min 30 s.

Weight of material as determined by radioisotope dilution flow = 8.61 ± 0.06 ton.
Weight of material by direct weighing = 8.632 ton.

Then

$$S_1 V = Q \int_0^t S_2 dt \tag{4}$$

giving $Q = S_1 VF/N$ (Total count method) or $\bar{Q} = S_1 VF/\bar{r}t$ (Continuous Sample method), where F is the efficiency of the counting set-up, S_1 is the specific activity of the injection solution, S_2 are the specific activities of the samples, Q is the volume flow rate, t is the time of sampling after tracer injection, N is the total number of counts accumulated, and \bar{r} is the counting rate for a homogenized sample.³² The flow rate can be determined either by sampling (total sample method) or simply by using a ratemeter and obtaining a count *versus* time trace at the sampling position (total count method). Neither method is as accurate as the dilution flow, but they are convenient in the measurement of large flows in open channels, *e.g.* effluent flow, as the amount of radioactivity required is much less than that used for the dilution flow method.¹⁸

Radioisotope measurements can provide an instantaneous method for the measurement of flow with an ease and accuracy that is difficult to achieve by other methods. The technique is widely used within the oil³³ and chemical industries, both for the measurement of unmetered flows and for the calibration of existing flowmeters. The checking of material balances within chemical plants usually depends ultimately on the accuracy of measurement of the flow rates of the materials entering and leaving the plant. In recent years the greatly increased legislation concerned with environmental conditions has led to a greatly increased demand for the measurement of flow in drains and open channels.

³² K. Ljunggren, Symposium on Radioisotope Tracers in Industry and Geophysics, IAEA, Prague, 1966, p. 303.
³³ D. F. Rhodes, *Instrumentation Technol.*, 1975, October, p. 43.

Leak Detection.³⁴—The ease of detection of radioactivity and the unambiguous nature of the qualitative determination of its presence make the use of radiotracers ideal for the detection and measurement of leaks. The methods used depend on the system under investigation but the techniques have been applied in situations ranging from underground pipelines²⁰ to heat-exchanger shells,²³ reactor cooling systems, and aircraft tyres.²¹ Leaks are often detected by the continuous injection of a radioactive tracer until the section within which the leak is suspected is uniformly labelled. The tracer within the pipe is then flushed away and a survey is conducted to detect any residual activity in the area adjacent to the pipeline or vessel which has escaped through leakage. It is often advantageous if, before flushing the pipeline to remove radioactivity, a valve is closed and the pipeline is pressurized. Detection of the residual activity from the leak may be carried out by the use of sensitive detectors by traversing the pipeline length or by the use of a pig containing a radioactivity detector which traverses the line within the pipe³⁵ and prints out the distance from the starting point whenever the radioactivity exceeds a predetermined threshold.

In chemical plants, which often involve a number of process units and heat exchangers, often the first indication of leakage problems is the production of off-specification material. It is obviously very desirable to isolate any leakage, so that the plant down-time may be minimized or avoided by the use of alternative equipment. In situations like this the leaks must be detected while the plant is on-line, and the technique generally used is the injection of a pulse of activity into the material (often cooling water) that is thought to be leaking followed by sampling of the product. This is carried out at a number of points until the position of the leakage is known to be within a single unit. Physical tracers can often be used for this type of study, e.g. ^{24}Na for the detection of leaks of cooling water, but care must be exercised in some cases where leakage may take place from the liquid or the gas phases, e.g. leaks of steam into process material, where negative results have been obtained using both a liquid (^{24}Na) and gaseous (^{41}A) tracer but a significant leak has been detected when a chemical tracer is used ($^3\text{H}_2\text{O}$). In this case it is obviously necessary that the tracer be compatible with both systems, *i.e.* the leaking material and the product material, a condition which is difficult to achieve with physical tracers.

Material Movement and Residence-time Distributions.—The way in which material moves through a processing unit must obviously have a profound effect on the quality of the final product obtained. Thus a study of the mode of matter transport within a given unit may greatly influence the mode of operation of that unit and also the design of any new units.

The simplest application of radioisotope techniques in this type of study is in the measurement of mixing times in a simple batch process. In this case a pulse of radioactivity is introduced into the mixing vessel and then samples are taken at intervals until the distribution of radioactivity within the system is uniform. The determination of mixing times obviously allows the most effective use to be made of expensive mixing equipment.

³⁴ M. Gerrard, *Isotopes and Radiation Technol.*, 1968, **6**, 443.

³⁵ G. Dorgebray (Elf Union) U.S. P. 3 778 613, 11th December 1973.

Residence-time Distributions. Applications of tracers in the assessment of mixing are trivial compared with the information that can be obtained by injection of a pulse of material into the process stream followed by monitoring of the pulse at a later stage in the process. The shape of the pulse may be analysed so that information is obtained about the movement of material in this part of the process.

In the chemical industry one frequently used model of the process system is that of stirred tanks or pots. The exit pulse is analysed in terms of the mean residence time (t_m) and the number of perfectly stirred pots (n) in a cascade which would produce the observed exit trace. For a closed system into which a pulse of radioactivity is injected (Δ function) the shape of the exit trace can be expressed as:

$$E(t) = \left[\frac{n}{t_m - t_1} \right]^n \left[\frac{(t - t_1)^{n-1}}{\Gamma(n)} \right] e^{-n[(t - t_1)/(t_m - t_1)]} \quad (5)$$

where $\Gamma(n)$ = Gamma function, t_1 = delay time, t = real time.

This simple analysis can be used where the data obtained are fairly crude. With modern injection and detectors the data are usually good enough to allow further analysis in terms of the moments of the residence-time probability density, E , of the tracer, derived from the moments of the input and output traces. In this analysis the input trace is not necessarily a Δ function. The various moments can be analysed for various situations,³⁶ e.g. open and closed pipes with axial diffusion, closed apparatus with gamma distribution and delay, and adsorption processes.³⁷ The analysis applied to the output curves depends on the information required, and various attempts have been made to gain detailed information from the tracers. Niemi³⁸ used a particulate ⁵⁹Fe tracer to study flotation processes in the metallurgical industry. The exit pulse is analysed by the method of least squares. An ideal injection impulse is assumed and the results are used to predict the behaviour of particles under varying conditions of process loading.

A simpler approach has been adopted in the determination of the residence times and the degree of mixing of coke and limestone in iron furnaces.³⁹ In the study of material movement of solids the choice of tracer is very important, as the behaviour of the material can depend on a number of parameters, e.g. density, particle size, and particle strength. The value of using reactor-irradiated process material has been demonstrated by a study on a ferrochrome smelter,^{40, 41} where the use of activated process material revealed that the pellets of chrome concentrate, the lump ore, the coke, the dolomite, and the quartz feeds to the preheater kiln all had different residence times, depending on the grain size of the particles. The knowledge of the residence time allowed several process developments to be carried out, resulting in a decrease in the amount of unusable product.

The continuous transport of material in the WORCA steelmaking process has been studied, using radioactive tracers [¹⁹³Au (steel-tracer) and ¹⁴⁰La (slag)] to follow the counter-current gravity flow of steel and slag.⁴² The process was treated

³⁶ R. E. Goddard, personal communication.

³⁷ E. Kučera, *J. Chromatog.*, 1965, **19**, 237.

³⁸ A. Niemi, ref. 14, p. 131.

³⁹ J. S. Michalik, Z. Bazaniak, J. Palige, K. Świgón, and M. Radiwan, ref. 14, p. 205.

⁴⁰ R. Kuoppamäki, J. Kuiesi, and S. Blomquist, ref. 14, p. 227.

⁴¹ A. Tamminen, Second European Conference of Triga Reactor Users, Pavia, September 1972.

⁴² T. A. Engh, L. Hansson, and K. Ljenggren, ref. 14, p. 251.

as a one-dimensional reactor, using the dispersion model.⁴³ A detailed analysis of the flow is given in terms of the Pedet number of the slag and the possible boundary conditions of the reactor.

Studies have also been made on the transport of matter through rotating centrifuge drums,⁴⁴ in the batch milling of gold ore—using various ore particle sizes,⁴⁵ in revolving furnaces (including the study of dust formation),⁴⁶ in rotating cement furnaces,⁴⁷ and in the cooling drum of a cement furnace, where again it was shown that variations in particle size have a large effect on the mixing and transport processes.⁴⁷ A general discussion on the use of radioactive tracers in the metals industry has been published.⁴⁸ The chemical industry makes extensive use of this type of technique, although little has been published.⁴⁹ Recent published studies have been carried out on a high-pressure hydrogenation unit (using a [¹⁴C]octadecanol tracer),²⁷ on some continuously operating polycondensation reactors,¹⁹ and in polyethylene production.⁵⁰

Although a large amount of information is obtainable from measurements of residence time, it is rare that the analyses have been carried to the full extent. Difficulties can arise by the use of incorrect assumptions as to the conditions present in the process; for example, most inlet and exit tracers are measured by detectors placed externally to the inlet and exit pipes. Thus, at the inlet, the assumption is usually made that the velocity profile across the pipe is flat and the tracer is adequately dispersed. If these assumptions are correct then the average tracer concentration as measured by the detectors is proportional to the fluid flux. If the velocity profile is not flat, or the tracer is not well dispersed, then the average concentration at the section may be grossly misleading. This is the case with a liquid in laminar flow in a pipe. Similar considerations apply to the exit trace, where again turbulent flow is necessary if an external detector or specific point-sampling device is used.

Mass-balance and Chemical Reaction Studies. If the material under study is undergoing chemical reactions during mixing and transport then it is obviously necessary to use a radioisotopic tracer which is chemically and physically identical to the material under study. The use of this type of tracer, coupled with the techniques described in the previous section, allows the chemical reactions occurring in a given residence time to be studied, and by an extension of these techniques the mass balances for a given element or compound may be determined.

The metallurgical industry has once again been at the forefront in applying these techniques. The use of neutron-activated lead–zinc sinter containing primarily ^{69m}Zn, ⁶⁵Zn, ⁷⁶As, and ¹²²Sb allowed the transport and distribution of zinc in the

⁴³ T. A. Engh, C.-E. Grip, L. Hansson, and H. K. Womer, *Jerkont. Annlr.* 1971, **155**, 553.

⁴⁴ A. van Dalen, *Polytech. Tijdschr., Procestech.*, 1974, **29**, 9.

⁴⁵ D. I. Exall and W. J. Taute, *Nuclear Sci. Abs.*, 1974, **29**, 12 993.

⁴⁶ I. Torok, *Izotopnitskaya*, 1974, **17**, 400.

⁴⁷ H. Rötzer and V. Meuhldorf, *Nuclear Sci. Abs.*, 1975, **31**, 14 260.

⁴⁸ Yu. B. Belyaev, 'Use of Radioisotopic Tracers for Investigation into Metallurgical Process', Atomizdat, Moscow, 1972 (*Nuclear Sci. Abs.*, 1975, **31**, 3606).

⁴⁹ P. Johnson, R. M. Bullock, and J. Whiston, *Chem. and Ind.*, 1963, **19**, 750.

⁵⁰ A. C. Castagnet, C. Czulak, M. Said, T. Chara, S. Nakahira, and R. A. Perablo, *Nuclear Sci. Abs.*, 1974, **30**, 23 590.

zinc phase, lead phase, and slag of an Imperial Smelting furnace to be determined.⁵¹ It was also possible to identify the chemical reactions occurring in the various sections of the furnace and to suggest various means of preventing the re-oxidation of zinc vapour within the furnace. A similar study has been carried out on the distillation and purification of zinc and cadmium during all stages of their production.⁵²

The mass balances of various elements (S, P, and Cr) in batch iron-making (open-hearth process) and continuous iron-making (Krupp-Reno process) have been studied.³⁹ The isotopes are injected as pulses of activity, and an attempt has been made to select a suitable chemical form for the tracer, although this presents a number of difficulties when dealing with complex feed materials such as fuel oil and pig-iron. A general method of dealing with the problems of multi-source and multi-product distributions in determining the mass balances has been presented.

In the determination of mass balances, two approaches are possible: (a) the pulse/total count method, in which a pulse of activity is injected and all product streams are sampled continuously and the total activity in each is determined, or (b) the continuous injection/steady-state method, in which tracer is injected over a period, to give a steady-state tracer concentration in the process, and then the mass balance is determined by sampling the product streams at the steady state and comparing their radioactive concentrations with the rate of injection of radioactivity. In general, the second method gives more accurate results and a smaller number of samples to be processed, but often the continuous nature and size of the process being investigated preclude the use of steady-state methods because the amount of tracer that would be necessary would be too large. Studies using both of these methods have been carried out on mechanisms in the deoxidation of steel⁵³ and in coking processes.⁵⁴

Mass-balance measurements are of prime importance in the chemical and petrochemical industry, and many problems have been studied using the techniques described above. The most useful isotopes are ^{14}C and ^3H , incorporated into labelled compounds. These isotopes present problems in that they are long-lived, low-energy β -emitters. Thus sampling is required, and the use of large quantities of radioactivity often presents problems of disposal. It is usually possible to arrange for the dilution of any radioactive product to acceptable levels, *e.g.* to below naturally occurring levels, and the use of low-level counting techniques which have been developed in connection with radiocarbon and tritium dating can greatly reduce the amount of isotope required.

Wear.—Wear processes and the means of reducing wear by the use of lubricants *etc.* are of great interest to most industrial concerns. Radioactive tracers and methods of analysis have played their part in the study of wear phenomena, especially in reducing the time required to carry out wear studies.

The most usual method of detecting wear is to activate the component under study either by neutron irradiation or by the use of accelerator-produced particles, *e.g.*

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⁵² K. Akerman, Eurisotop-84, December 1973 (*Nuclear Sci. Abs.*, 1974, **29**, 26 954).

⁵³ H. Litterscheidt and D. Lohr, Eurisotop-89, June 1974 (*Nuclear Sci. Abs.*, 1975, **31**, 663).

⁵⁴ J. Siewierski, H. Kolaski, and H. Firganek, *Isotopenpraxis*, 1974, **10**, 174.