

NO9100128

IFE/KR/E-91/009

**SELECTION OF TRACERS FOR OIL  
AND GAS RESERVOIR EVALUATION**

by

**Tor Bjørnstad**

IFE/KR/E-91/009

SELECTION OF TRACERS FOR OIL  
AND GAS RESERVOIR EVALUATION

by

Tor Bjørnstad

ISSN 0333-2039  
ISBN 82-7017-113-1

August 1991  
Institutt for energiteknikk, Kjeller, Norway

PERFORMING ORG. Institutt for energiteknikk P.O.Box 40 N-2007 Kjeller Norway		DOCUMENT NO. IFE/KR/E-91/009	
PROJECT NO./CONTRACT NO.		DATE August 1991	
PROJECT NAME		CLIENT/SPONSOR ORG.	
		SPONSOR'S REF.	
TITLE AND SUBTITLE SELECTION OF TRACERS FOR OIL AND GAS RESERVOIR EVALUATION			
AUTHOR(S) Tor Bjørnstad <i>Tor Bjørnstad</i>		REVIEWED	APPROVED <i>J. Nittberg</i> Jan Nittberg
ABSTRACT <p>The importance of tracer tests in reservoir description is increasingly acknowledged by reservoir engineers as a method to obtain valuable dynamic information from the reservoir. The present article is a "state-of-the art" report on tracer technology for interwell investigations. Experiences gained from a number of reported field tracer tests are reviewed, and results from detailed laboratory investigations on the static and dynamic behavior of various tracer molecules are discussed. A critical evaluation of the applicability of the various identified tracers is provided. Present and future trends in the development of tracer technology for reservoir description are sketched.</p>			
KEY WORDS Water tracers, gas tracers, radioactive, non-radioactive, oil reservoir, interwell, review article.			
CLASSIFICATION AND/OR SUBJECT GROUP UDC 621.039.85: 622.276			
INDEX SYSTEM/THESAURUS TERMS ETDE: Tracer techniques; Oil wells; Oil fields; Natural gas wells; Radioactive tracer logging; Field tests; Reservoir engineering; Reviews.			
SUPPLEMENTARY BIBLIOGRAPHIC DATA		ISSN 0333-2039	
		ISBN 82-7017-113-1	
		NO. OF PAGES 43	
AVAILABILITY: THIS DOCUMENT/THIS PAGE Open / Open		LANGUAGE: DOCUMENT/SUMMARY English / English	
DISTRIBUTED BY Institutt for energiteknikk		RECIPIENT'S NOTE	
PRICE			

## TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1. INTRODUCTION	1
2. PREVIOUS EXPERIENCES	1
3. PURPOSES OF TRACER TESTS	2
4. TRACER SELECTION CRITERIA	2
5. TRACER TYPES	2
5.1. Isotopic ratios	3
5.2. Radioactive atoms or molecules	3
5.3. Non-radioactive chemical tracers	3
6. TRACERS FOR INJECTED WATER	3
6.1. Isotopic ratios	4
6.2. Radioactive atoms or molecules	4
6.2.1. Neutral (non-charged) atoms	4
6.2.2. Anionic tracers	5
6.2.2.1. Small-scale behavior	5
6.2.2.2. Requirements and limitations for field use	6
6.2.3. Cationic tracers	8
6.2.3.1. Small-scale behavior	8
6.2.3.2. Field application	9
6.3. Non-radioactive (or chemical) tracers	9
6.4. Water tracers,- summary and recommendations	11

Table of content continues:

<u>Section</u>	<u>Page</u>
7. TRACERS FOR INJECTED GAS	11
7.1. Non-radioactive isotopic tracers	12
7.2. Radioactive molecules	12
7.2.1. Inorganic gases	12
7.2.1.1. Small-scale behavior	13
7.2.1.2. Requirements for field applications	13
7.2.2. Organic gases	14
7.2.2.1. Small-scale behavior	14
7.2.2.2. Tracer molecule degradation	15
7.2.2.3. Field application	16
7.3. Non-radioactive chemical tracers	16
7.3.1. Polyhalogenated hydrocarbons	16
7.3.2. Perfluorinated hydrocarbons	17
7.3.2.1. Small-scale behavior	17
7.3.2.2. Field application	18
7.4. Gas tracers,- summary and recommendations	19
8. CONCLUSION AND FUTURE DIRECTION OF DEVELOPMENT	19
REFERENCES	21
TABLES	25
FIGURE CAPTIONS	31
FIGURES	32

## 1. INTRODUCTION

In addition to the information inherent in the production profiles of the various reservoir fluids, dynamic information from a reservoir may in principle be obtained by two methods: Pressure testing and tracer testing.

The value and importance of tracer tests is increasingly acknowledged by reservoir engineers. For petroleum reservoirs on the Norwegian continental shelf this awareness materializes in a growing demand for practical implementation of tracers for reservoir characterization.

This demand will have to be met with the present state of knowledge of tracer behavior and interactions. This knowledge will be summarized here, and restricted to those tracers which may be applied in interwell gas and water tracing for reservoir evaluation purposes.

Towards the end of the chapter, we will speculate somewhat into future extended possibilities in interwell tracer applications.

## 2. PREVIOUS EXPERIENCES

The present state of tracer knowledge is gained through dedicated laboratory investigation programs<sup>1-12)</sup>, through oil field experiences<sup>13-46)</sup>, ground-water movement investigations<sup>47-49)</sup>, atmospheric tracing experiments<sup>50,51)</sup> and also to a significant degree through the work carried out on migration of radioactive species in soil for the purpose of evaluating radioactive waste repository sites<sup>52)</sup>.

Although the integrated knowledge from these areas is substantial, the information achieved is not always consistent. Results from one area of investigation cannot readily be transferred to new fields because of both scaling problems and changing experimental conditions. However, the views conveyed here on tracer behavior is based on an extract of the most reliable and consistent investigations from the fields referred above, and constitutes as such the present state of tracer behavior knowledge.

### 3. PURPOSES OF TRACER TESTS

The primary goals with the interwell tracer tests reported in the literature may be summarized as follows:

- a. Depiction of flow directions and interwell connections.
- b. Evaluation of volumetric sweep efficiency between injector and producer.
- c. Detection and evaluation of permeability stratification.
- d. Detection of faults and barriers to flow.

There is also a beginning activity for:

- e. Estimation of average residual oil saturation.
- f. Estimation of average ion exchange capacity.
- g. Evaluation of changing imbibition potential.
- h. Evaluation of the effect of reservoir chemical treatment.

### 4. TRACER SELECTION CRITERIA

For unambiguous single-phase tracing of either the water or the gas phases in enhanced oil recovery, the following tracer selection criteria apply to added tracers:

- a. Insignificantly degradable under injection, reservoir and production conditions (i.e. high thermal, chemical, physical and microbiological stability).
- b. Must follow passively the labelled phase without unforeseen or undesired interactions.
- c. Insignificant unwanted natural occurrence in involved fluids.
- d. Detectable in very low concentrations.
- e. Toxicity/radiotoxicity at an acceptable level.
- f. Non-problematic logistics and handling.
- g. Sufficient commercial availability.
- h. Acceptable cost.

### 5. TRACER TYPES

There are in principle three types of tracers available:

- a. Stable-isotope ratios.
- b. Radioactive atoms or molecules.
- c. Non-radioactive chemical compounds.

The main characteristics of each of these types are briefly given below.

### 5.1. Isotopic ratios

A prerequisite for application of this type of tracer is the existence of a significant (and in reality naturally occurring) difference of the isotopic ratio in question between the injected fluid and the reservoir fluids. Accordingly, the accuracy and sensitivity of the method depends on a good characterization of the initial fluids and on the actual size of the isotopic ratio difference, respectively.

The isotopic ratios are readily measured with sensitive mass spectroscopy techniques.

### 5.2. Radioactive atoms or molecules

Radioactive species are probably the most frequently used tracers in well-to-well tests. Their main advantage is their extremely low detection limits. Depending on the particular radioactive species in question, they may be detected in concentrations from a few thousand atoms per liter and upwards.

For beta-particle and electron emitting tracers the main detection method will be liquid scintillation counting or gas proportional counting (for gaseous species). For tracers which emit gamma or x-rays, the detection technique high-energy (gamma, x-ray) electromagnetic radiation spectroscopy with solid scintillation or semiconductor detectors.

### 5.3. Non-radioactive chemical tracers

Non-radioactive molecules with good survival characteristics at reservoir conditions may also be applied for fluid tracing. However, the requirement of high detection sensitivity apply also here. Although the sensitivity for chemical species normally is several orders of magnitude lower than for radioactive species, the lower cost of the non-radioactive material allows injection of higher quantities to partly compensate for the lack of sensitivity. However, if the molecule shall comply with the requirement of non-interaction with fluids and rocks, the amount injected can obviously not be unlimited. Therefore, the main targets for chemical tracers have traditionally been smaller land-based reservoirs with short (less than a few hundred meters) well spacing.

The analysis of the chemical tracers have been reported to be carried out by gas and liquid chromatography (GC and HPLC), nuclear magnetic resonance (NMR), ion chromatography (IC), colorimetry, fluorometry and neutron activation analysis (NAA).

## 6. TRACERS FOR INJECTED WATER

A substantial number of field tests involving water tracers have been reported in the literature (see ref.s 13-29,38,44,45 and references therein). This chapter will discuss the experimental experiences with petroleum reservoir water tracers.



## 6.1. Isotopic ratios

To our best knowledge, none of the reported field tests have included isotopic ratio analysis as a main tool.

The isotopic ratios that are directly applicable as tracers are the naturally occurring  $^3\text{H}/^1\text{H}$  (D/H) and the  $^{18}\text{O}/^{16}\text{O}$  ratios in the water molecules measured as the  $\delta\text{D}$  and the  $\delta^{18}\text{O}$  values. For some North Sea reservoirs a sensitivity limit of 0.5-1% content of injection water into formation water has been established. This sensitivity limit could in principle be lowered by addition of enriched heavy water,  $\text{D}_2\text{O}$ , to the injection water. However, due to the relatively high natural occurrence of deuterium (0.015%), the needed amount of heavy water (tons) to give a substantial sensitivity increase would be economically prohibitive. In general, the cost of isotopically enriched material is too high to be of real interest for interwell tests. However, this method has higher actuality in single-well push-and-pull operations.

## 6.2. Radioactive atoms or molecules

Most of the tests referred above involve radioactive tracers<sup>13-17,20-22,24,25,27-29,38,44,45</sup>. These tracers may be further subdivided into three classes, neutral, anionic and cationic tracers. These have different behavior and interactions on the microlevel in a porous medium. However, applicable tracers have been found in all three classes.

### 6.2.1. Neutral (non-charged) atoms.

*Tritiated water*, HTO, is a neutral atom and the most widely trusted and applied water tracer in reservoir evaluation tests. It represents a water tracer probably as close to ideality as practically achievable. The small, though significant, differences in physical parameters like the vapor pressure (lower than for  $\text{H}_2\text{O}$ ) and the diffusivity (also lower than for  $\text{H}_2\text{O}$ ) become insignificant in a dynamic experiment in a reservoir. It is usually referred to as a *standard reference water tracer* against which the behavior of all other tracer candidates are measured.

The detection limit with state-of-the-art liquid scintillation counting equipment in direct counting after a distillation step is  $L_D(\text{HTO}) = 2 \text{ Bq/l}$  based on a counting time of 4 hours and 8-10 ml water in the counting sample. It is possible to lower the  $L_D(\text{HTO})$  by a factor of up to 36, corresponding to 0.06 Bq/l, by electrolytic enrichment. However, there is a limit to the practical use of enrichment, especially when sea water is the base of the injection water. Tritium is a cosmogenic radionuclide. In the ocean surface waters concentrations in the order of 1-30 tritium units (TU), corresponding to 0.12 - 3.6 Bq/l, may be found<sup>53</sup>. This natural concentration sets the limit on the  $L_D$  of any added HTO.

Normally, the total amount of HTO needed in an interwell pulse injection test ranges between 0.37 - 11 TBq (10-300 Ci), in North Sea operations between 3.7 - 11 TBq.

So far, HTO is the only neutral radiotracer for water which has found any application in oil reservoirs. Others with potential application like tritiated ethanol and its light homologous molecules have been subject to limited tests in the laboratory. Substantial microbial degradation was experienced. However, experiments under controlled anaerobic conditions and with a microbial flora experienced in off-shore operations should be conducted. A number of other radiolabelled aliphatic and aromatic hydrocarbons (alcohols, ketones) and radiolabelled polyfluorinated hydrocarbons should be subjected to the same test sequence. A substantial research program including this kind of tests is underway in the authors laboratory.

### 6.2.2. Anionic tracers

From laboratory and field experience one may conclude so far that near-ideal water tracers are most likely to be found among the anionic species.

To date, established anionic radiotracers for sandstone reservoirs are the halides  $X^-$ , the pseudohalide  $SCN^-$  and, with reservation, the very stable complex  $Co(CN)_6^{3-}$  ( $K = 10^{64}$ )<sup>52</sup>, and conditionally also  $SO_4^{2-}$ . Half-life considerations limit the halide tracers to  $^{36}Cl^-$  ( $t_{1/2} = 3.0 \cdot 10^5$  y) and  $^{125}I^-$  ( $t_{1/2} = 60$  d).  $SCN^-$  may be labelled with both  $^{14}C$  ( $t_{1/2} = 5730$  y) and  $^{35}S$  ( $t_{1/2} = 87$  d) to give  $S^{14}CN^-$  and  $^{35}SCN^-$ .  $Co(CN)_6^{3-}$  may be labelled with the five different radionuclides  $^{56}Co$  ( $t_{1/2} = 79$  d),  $^{57}Co$  ( $t_{1/2} = 271$  d),  $^{58}Co$  ( $t_{1/2} = 71$  d),  $^{60}Co$  ( $t_{1/2} = 5.22$  y) and  $^{14}C$  to the corresponding tracer molecules  $^{56}Co(CN)_6^{3-}$ ,  $^{57}Co(CN)_6^{3-}$ ,  $^{58}Co(CN)_6^{3-}$ ,  $^{60}Co(CN)_6^{3-}$  and  $Co(CN)_5(^{14}CN)^{3-}$ .  $SO_4^{2-}$  may be labelled with  $^{35}S$ .

For limestone the same range of tracers is expected to be applicable. An extensive laboratory investigation is underway in the authors laboratory to examine this question in detail.

Below we will document these conclusions with experimental evidence partly established through comprehensive laboratory experiments where the SPOR program has played a major role, and partly through field experiences.

#### 6.2.2.1. Small-scale behavior

On smaller scale the anionic tracers behave slightly different from the ideal tracer HTO in a sandstone matrix. Their dynamic behavior has been examined in a number of controlled flow experiments carried out under simulated reservoir conditions. Sandstone cores of Clashack, Berea and Gullfaks reservoir material have been used, both as 1.5"x3" ( $\phi$ xl) consolidated plugs and as 200 cm long columns packed with the crushed material. In some of the experimental series the porous material has been saturated with synthetic formation water (Gullfaks), in others the porous medium has been prepared to residual oil saturation by using, for simplicity, decane as the oil phase. The tracers under examination have been dispersed together with HTO in a small volume ( $\approx 700 \mu$ l) and injected as a narrow pulse into the core with synthetic injection water. In most of the experiments the flowrate has been kept at realistic reservoir values with frontal advantage rates of 0.3 - 0.5 m/d. Some experiments have been conducted with increased flowrates to simulate the conditions in the vicinity of a well. Other experimental parameters have been a

pressure of 230 - 250 bar and a temperature of 90 °C.

Samples of the effluent were collected and analyzed, and the normalized dispersion profiles derived for the various tracers. Examples of dispersion profiles for carrierfree  $S^{14}CN^-$  + HTO are given in fig.1 and fig.3 for watersaturated and residual oil containing cores, respectively. From fig.1 it is apparent that the two tracers behave very similar. However, any small difference may be "artificially" amplified by subtraction of the two normalized curves. The resulting curve, fig.2, may tentatively be explained by electrostatic repulsion between  $S^{14}CN^-$  and the negatively charged surfaces of the mineral grains in the porous medium. This repulsion causes first  $SCN^-$  in each delta-element of the tracer pulse to hesitate in entering the core, then, when first entered, to flow preferentially in the center of the main flow channels. Thus,  $SCN^-$  does not follow closely the "free" movement of the water molecules, for instance by diffusion in and out of dead-end pores and through narrow flow channels. The net result is that the total  $SCN^-$  tracer pulse has a shorter transit time through the core than HTO. This fast-running tendency is further confirmed in the experiments with residual oil in the core. In a water-wet sandstone core the oil will mainly be distributed as droplets in the center of the flow channels. Accordingly, the water-dissolved anionic species are forced to flow closer to the grain surfaces and thus experience a stronger integrated repelling force causing the relative effective volume available for anionic flow to be still smaller. This results in still faster transport as shown in fig.4.

These results are reproduced consistently in a number of experiments both on small cores and larger columns. Interestingly enough, qualitatively the same behavior is found for  $^{36}Cl^-$ ,  $^{125}I^-$  and  $^{35}SO_4^{2-}$ , although the transport of the latter seems to be somewhat more complex.

We believe that the effect described here, also called the ion exclusion effect, is largely smeared out on field scales by the sizable macroscopic dispersion in a complex reservoir. Though, the repelling force will counteract eventual sorption reactions to positively charged binding sites in the minerals and, therefore, support and promote the flooding properties of the anions, thus resulting in a dynamic behavior close to that of HTO and the water itself.

#### 6.2.2.2. Requirements and limitations for field use

Both  $S^{14}CN^-$ ,  $^{36}Cl^-$  and  $^{125}I^-$  have been injected in the North Sea reservoirs on the Norwegian continental shelf, the two first in on-going experiments not yet published, and the latter in a pilot waterflood at Ekofisk<sup>28)</sup>.

For  $S^{14}CN^-$ , the amounts needed for good-sensitivity tests in the North Sea reservoirs lies in the range 15 - 40 GBq (0.4 - 1.1 Ci) and for  $^{35}SCN^-$  and  $^{125}I^-$  the same range or slightly higher depending on the expected length of the test. This range is determined by the analytical sensitivity of the tracers in produced brine. A detection limit of  $L_D(S^{14}CN^-) = 0.005$  Bq/l has been achieved<sup>54)</sup> with liquid scintillation counting when a chemical enrichment based on anion exchange separation is carried out on an original sample volume of 1000 ml and a counting time of 4 hours is applied.  $L_D(^{35}SCN^-)$  has the same value.

$^{125}I^-$  may be analyzed both by gamma-ray spectroscopy and by liquid scintillation counting. For the former method the sensitivity by direct counting of a 1000 ml sample in so-called Marinelli

geometry with a 5x5" NaI(Tl) solid scintillation planar detector has been measured to  $L_D(^{125}I) = 0.14 \text{ Bq/l}^{255}$ . A factor of  $\approx 6$  in the  $L_D$  may be gained when I is separated chemically and concentrated to a small volume by precipitation as AgI(Ag<sup>125</sup>I) and counted on a well-type NaI(Tl) detector. With liquid scintillation counting an additional factor of 2 - 5 may be gained.

For  $^{36}\text{Cl}$ : the situation is different. This a cosmogenic radionuclide, and it is also continuously produced by neutron capture reactions on naturally occurring chlorine ( $^{35}\text{Cl}$ ) in the earth crust where the neutron source is mainly the spontaneous fissioning nuclide  $^{235}\text{U}$ . The natural occurrence in surface waters may range from  $\approx 10 \cdot 10^{-15}$  to more than  $1000 \cdot 10^{-15}$  atoms  $^{36}\text{Cl}/\text{atom Cl}$ . Its long half-life and limited availability on a world basis and, accordingly, a high cost, makes injections of the 15 - 40 GBq needed for standard liquid scintillation analysis nearly prohibitive. However,  $^{36}\text{Cl}$  may not only be analyzed by its radioactivity, but also by accelerator mass spectrometry<sup>56</sup>. It is a sophisticated (and correspondingly expensive) analytical technique capable of "counting single atoms". It has originally been developed for dating purposes by utilizing the naturally occurring cosmogenic nuclides. If a field experiment is based on this analytical technique which has an  $L_D(^{36}\text{Cl}) \approx 10^{-15}$  atoms/atom, the needed amount for injection may be as low as 1.5 GBq ( $\approx 40 \text{ mCi}$ ) corresponding to  $2 \cdot 10^{22}$  atoms ( $\approx 1.2 \text{ g}$ ) of  $^{36}\text{Cl}$ .

For the  $\text{Co}(\text{CN})_6^{3-}$  complex with its three negative charges, one would expect, if the ion exclusion theory is correct, a still stronger electrostatic repulsion manifested in an even more rapid breakthrough or narrower dispersion profile in laboratory experiments of the type described above. Such experiments have not yet been conducted, but will be carried out relatively shortly.

On the other hand, one has gained a lot of experience with this complex the hard way. It has been used with various radioactive labels rather extensively in real field tests<sup>20,21,24,25</sup> with encouraging results. However, a non-published incident where the use of  $^{60}\text{Co}$ -labelled complex has contaminated the injection tubing has given rise to some skepticism about this tracer which has hampered its use. We suspect that the contamination may be due to radiochemical impurities where the  $^{60}\text{Co}$  label also was present in other and less stable chemical forms. This problem is for the moment under investigation. Until an explanation has been found and proven experimentally, this tracer should remain on the waiting list. A positive outcome of these investigations is, however, probable.

Analysis of samples containing only one type of the radioactive cobalt isotopes may be carried out either by gamma spectroscopy directly on the collected samples without any sample preparation needed, by close-geometry single gamma or coincidence summing gamma ( $^{60}\text{Co}$ ) spectroscopy on small samples separated from large (1 - 2 l) liquid volumes for instance by anion exchange or by liquid scintillation counting (also after activity enrichment and volume reduction).

Samples containing mixtures of different Co-isotopes have to be analyzed with different gamma-spectrometric methods (including high resolution spectrometry).

The  $^{14}\text{C}$ -labelled tracer has to be measured by liquid scintillation counting. It has not yet been examined whether or not this tracer can be analyzed in mixtures with the corresponding radiocobalt labelled tracer molecules.

Exact detection limits for the various tracers of this kind have not yet been established. A development program is underway in the author's laboratory. However, the sensitivity will

probably lie in the range between 0.1 - 0.005 Bq/l for the various methods based on realistic counting times and a  $3\sigma$  criterion on the  $L_D$ .

Needed amounts for these tracer molecules for North Sea reservoirs will be in the range 5 - 40 GBq ( $\approx 150\text{mCi} - 1\text{ Ci}$ ).

$^{35}\text{SO}_4^{2-}$  has, to our knowledge, never been used in interwell tests although it may be a potential tracer. A prerequisite is, however, that sulphate-containing injection water has to be used. In addition, if the formation water contains a substantial concentration of  $\text{Ba}^{2+}$ , the start of the water injection will have to precede the tracer injection by at least 2 - 3 weeks. Thus, the barium is "neutralized" by precipitation or formation of undissociated molecules of the form  $\text{BaSO}_4$ .

The detection limit is  $L_D(^{35}\text{SO}_4^{2-}) \approx 0.01\text{ Bq/l}$ , thus requiring 15 - 40 GBq for pulse injection.

### 6.2.3. Cationic tracers

Tracer molecules with positive charges have so far not found any important application in interwell tests although a few have been tried in field experiments. Examples are  $^{63}\text{Ni}^{2+}$  ( $t_{1/2} = 100\text{ y}^{24}$ ) and  $^{85}\text{Sr}^{2+}$  ( $t_{1/2} = 65\text{ d}^{21}$ ). The former was never detected in a production well in consistence with later laboratory sorption experiments where  $^{63}\text{Ni}^{2+}$  was found to sorb relatively strongly onto Clashack sandstone<sup>55</sup>. The latter seems to exhibit reasonably good flooding properties. However, it has not been thoroughly tested in controlled experiments at varying simulated reservoir conditions and compared to HTO. If such forthcoming tests should support the positive view of  $\text{Sr}^{2+}$ , the most applicable isotope for long-term tests will be  $^{90}\text{Sr}^{2+}$  ( $t_{1/2} = 28.5\text{ y}$ ). In addition to the two mentioned radionuclides, some serious interest has concentrated on  $^{22}\text{Na}^+$ .

#### *6.2.3.1. Small-scale behavior*

Controlled laboratory experiments of the same type as described in section 6.2.2.1. have been carried out also on  $^{22}\text{Na}^+$  ( $t_{1/2} = 2.6\text{ y}$ ) where HTO was used as a reference tracer as usual. The dispersion profiles and the corresponding difference curve is displayed in fig.5 and 6, respectively. A genuine Gullfaks sandstone core, corresponding synthetic formation water and injection water which basically is filtered sea water have been used. As can be seen from fig.6,  $^{22}\text{Na}^+$  shows a slight retardation compared to HTO due to sorption (reversible ion exchange) to negative binding sites in the rock matrix. The curve is nearly a mirror image of the corresponding curve for  $\text{S}^{14}\text{CN}^-$  in fig.2. Due to the high sodium content in the injection sea water, however, the sorbed  $^{22}\text{Na}^+$  ions will readily be exchanged with corresponding inactive ions. The exchange rate is rapid and the delay correspondingly small.

The effect increases when the core has a residual oil saturation as shown in fig.s 7 and 8. This increase is due to the stronger average electrostatic interaction, and is consistent with the results referred above for  $\text{S}^{14}\text{CN}^-$  in fig.s 3 and 4.

### 6.2.3.2. Field application

Successful field use of  $^{22}\text{Na}^+$  will require a relatively high salinity of both the formation water and the injection water. Concentrations of the same order as found in sea water (2-3 % salt) is sufficient.

The minor relative delay measured in laboratory experiments will, however, probably persist and be significantly measurable in field experiments too. Nevertheless, one may conclude from the experience gained so far that  $^{22}\text{Na}^+$  may be used as a near-ideal tracer in sandstone reservoirs, and probably also in carbonate reservoirs.

Even if  $^{22}\text{Na}^+$  has been evaluated several times as an actual candidate for planned tracer injections in North Sea reservoirs, it has to date not been injected. The main reason is probably its relatively high price (comparable to  $^{36}\text{Cl}^-$ ) for the 15 - 40 GBq required for a long-term test.

$^{22}\text{Na}$  decays by emission of positrons followed by annihilation and gamma radiation. Accordingly, the analysis in produced brine is best carried out by gamma spectroscopy.

Optimized analysis of  $^{22}\text{Na}^+$  has been rather extensively studied<sup>57)</sup>. It was found that a detection limit of  $L_D(^{22}\text{Na}^+) = 0.15 \text{ Bq/l}$  may be achieved in direct counting without any sample pretreatment under the following conditions: A sample volume of 2000 ml in Marinelli geometry (see fig.9), a 5x5" NaI(Tl) detector, a counting time of 3 h, integration of the 511 keV annihilation peak and a  $3\sigma$  criterion on  $L_D$ . An additional factor of 2 can be gained when all salt is separated from the liquid sample, formed into a small-volume salt disc and counted on a planar 3x3" NaI(Tl) detector. When advantage is taken of the emitted coincident electromagnetic radiation (annihilation radiation and gamma), a further improvement is possible. The salt pellet may be counted in a  $4\pi$  "total absorption" spectrometer resulting in a detection limit of  $L_D(^{22}\text{Na}^+) = 0.06 \text{ Bq/l}^{57)}$ .

### 6.3. Non-radioactive (or chemical) tracers

Several reported field tests have included non-radioactive chemical tracers<sup>14-19,22,23,25,28)</sup> mainly being anions and non-charged watersoluble organic molecules. Examples of anions are  $\text{NO}_3^-$ <sup>15,17-19,22,38)</sup>,  $\text{Cl}^-$ <sup>23,26)</sup>,  $\text{Br}^-$ <sup>17,18)</sup>,  $\text{I}^-$ <sup>17,19,25,25)</sup>,  $\text{SCN}^-$ <sup>16-19,22,23)</sup>,  $\text{HBO}_3^-$ <sup>14)</sup> and  $\text{B}_4\text{O}_7^{2-}$ <sup>17,18)</sup>. Examples of organic molecules are fluorescein<sup>14)</sup>, rhodamine B<sup>14)</sup>, methanol<sup>16)</sup>, ethanol<sup>16,17)</sup> and isopropylalcohol<sup>15,17,22,38)</sup>.

There are also indications from a field test<sup>28)</sup> that cations may be used under certain conditions. One such cation is potassium,  $\text{K}^+$ . The accuracy depends on the maturity of the flood: Chromatographic delay of the tracer due to reversible sorption on rock surfaces are most prominent in the start of the flood and is thereafter gradually reduced.

The amount of tracer chemical needed for injection depends as usual on the sensitivity of the analytical technique and on the total estimated dilution volume for the tracer between injector and producer, but also to a significant degree on the level of naturally occurring tracer species. The

conditions may be rather different from reservoir to reservoir. Therefore, no specific rules or limits can be given, and each planned tracer test has to be evaluated individually. However, as a general guide a few examples are given below on published data on this topic for the most interesting tracer chemicals, mainly from smaller land-based reservoirs with well spacing in the range 30 - 100 m.

$\text{NO}_3^-$  has been injected continuously (0.3 pore volumes, PV) in concentrations of  $\approx 300$  ppm (as  $\text{NH}_4\text{NO}_3$ )<sup>19</sup> and as slug injection in a total amount of 4.5 tons<sup>17</sup>. Although biodegradation had apparently reduced the total concentration, the ion was clearly detected in producers.

$\text{Cl}^-$  and  $\text{Br}^-$  are normally of less use as added tracers due to high natural concentrations in formation and injection brine. In specific cases these tracers have been used in continuous concentrations of 5000 ppm<sup>23</sup> (as  $\text{NaCl}$ ) and 350 ppm<sup>19</sup> (as  $\text{NaBr}$ ), respectively, with positive results.

$\Gamma^-$  as  $\text{KI}$  has been injected in amounts of 170 - 635 kg<sup>17,19</sup> and been positively identified in production wells without any noticeable sorption or degradation.

$\text{SCN}^-$  has been injected continuously in concentrations of 300 - 1000 ppm (as  $\text{NH}_4\text{SCN}$ ) to a total mass of up to 1150 kg<sup>16,17,19</sup>. The performance has in general been satisfactory.

$\text{HBO}_3^-$  injected in concentrations of  $\approx 100$  ppm (as  $\text{H}_2\text{BO}_3$ ) over a few hours and  $\text{B}_4\text{O}_7^{2-}$  in concentrations of 700 ppm for 0.3 PV injected in small landbased reservoirs were never detected in a production well<sup>14,19</sup>.

Fluorescein and rhodamine B were simultaneously injected in a small land-based reservoir in amounts of 55 - 500 g<sup>14</sup>. The first was positively identified in a production well while the latter was never regained.

Methanol and ethanol injected continuously in a concentration of 1400 ppm<sup>16</sup> or as a slug with as much as 47.3 m<sup>3</sup> (well distance or dilution volume not given)<sup>17</sup>, were clearly produced in good yield although some degree of bacteriological degradation was experienced.

Isopropanol, also with an injected amount of 47.3 m<sup>3</sup>, seems less prone to bacteriological attack, and was readily produced in good yield in production wells.

From this brief review one may conclude that a number of already field-tested inorganic and organic ions and molecules are conditionally useful as reservoir water tracers in small reservoirs or in pilot areas where the well spacing or the total dilution volume is relatively small.

What are the prospects for these tracer chemicals in larger reservoirs with typical well spacings around 1000 m? In a land-based reservoir with well spacings 800 - 1000 m 109 tons of  $\text{NH}_4\text{NO}_3$  were injected<sup>15</sup>. Break-through had not occurred at the time of publishing. In any case, with such large amounts a number of practical operations become more difficult, especially on off-shore platforms with weight and space limitations. In addition, the  $\text{NO}_3^-$ , being one of the major components in the injection water, will hardly comply with the requirement of behaving passively in the water flow, at least in the vicinity of the wells.

If, for instance, the use of  $\text{SCN}^-$  was to be scaled up from the previously mentioned smaller-scale reservoir experiences to the North Sea conditions, 115 tons of  $\text{NH}_4\text{SCN}$  would be needed for one injection. These large masses are impractical to handle and their use as tracers will in practice be prohibitive.

However, better analytical techniques may turn this conclusion around. With the enrichment technique developed in ref.54 for  $\text{SCN}^-$ , a reduction with a factor of 10 - 50 is probably already within reach for  $\text{SCN}^-$ .

#### 6.4. Water tracers,- summary and recommendations

Table 1 concentrates the present state of knowledge about the applicability of water tracers, and gives, on this basis, recommendations for use. Some of the tracers mentioned should not be applied together in the same test since their individual analysis may be precluded. This is true for  $^{35}\text{SCN}^- + \text{S}^{14}\text{CN}^-$  where both must be counted by liquid scintillation technique and have very nearly the same beta energy, radiolabelled thiocyanates and radiolabelled cobalthexacyanides since the separation technique now applied for  $\text{SCN}^-$  does not exclude a simultaneous separation of the  $\text{Co}(\text{CN})_6^{3-}$ , and  $\text{Co}(\text{CN})_5(^{14}\text{CN})^{3-} +$  gamma-radioactive cobalthexacyanides since the first will have to be counted with liquid scintillation spectroscopy which will also respond to the presence of the others. At present it is unclear whether the spectral separation in the scintillation spectra is sufficiently large to allow simultaneous counting with good efficiency. These problems are largely a matter of analytical development, and may probably be resolved without substantial difficulty.

### 7. TRACERS FOR INJECTED GAS

Injection gases may roughly be divided into three types,- natural gas (or lean gas) composed mainly of methane and its light homologous gas molecules, nitrogen and carbondioxide. The gases behave differently in the reservoir. This behavior is mainly determined by their different critical values on temperature and pressure and their different solubility in the oil and water phases at reservoir conditions.

A further complexity to this picture is added by the fact that even the individual components in the natural gas behaves differently. This is the reason why one can hardly claim that there exists an ideal gas tracer for injected gas in general. Only for pure  $\text{CO}_2$ -injection, the radioactive  $^{14}\text{CO}_2$  may serve as an ideal tracer.

Much of the existing knowledge on gas tracers has been gained through field experiments, most of which have been of the inject-and-observe type without much a priori information on their relative behavior. Examples of reported field experiments are found in refs 15,30-46. Interesting and potentially useful information has emerged from atmospheric transport experiments<sup>50,51</sup>. Recently, controlled laboratory experiments under simulated reservoir conditions have added important and detailed information on gas tracer relative behavior<sup>11,12</sup>.



In principle, there are also three types of gas tracers available, - non-radioactive isotopic tracers, radioactive molecules and non-radioactive chemical molecules. The various types are treated briefly below.

### 7.1. Non-radioactive isotopic tracers

An example of a potential isotopic tracer for oil reservoirs is the methane molecule  $^{13}\text{CD}_4$  where all hydrogen atoms are exchanged with deuterium. This molecule is practically non-existent in natural methane. Thus, one of the main tracer requirements is fulfilled. It has never been reported used as a tracer in sub-surface gas tracing, but has successfully been applied to monitor long-range (155 - 2500 km) air transport in USA after release of only 84 g of the substance to the atmosphere<sup>58</sup>. The practical implementation for gas tracing by  $^{13}\text{CD}_4$  in oil reservoirs depends probably on the cost of sufficient amounts of the gas which again is determined by the analytical sensitivity. Updated values of these parameters are not known to the author at present. A somewhat poorer though cheaper alternative to  $^{13}\text{CD}_4$  is  $\text{CD}_4$  (with naturally occurring carbon).

Tracers of this kind are not yet ready for the reservoir, but should be investigated as a possible future alternative.

### 7.2. Radioactive molecules

A number of tracer tests incorporating radioactively tagged gas tracers have been reported in the literature<sup>31-40,42-46</sup>. The tracers fall into two groups. The first comprises the inorganic gases with tritiated hydrogen and the noble gases. The second group is composed of organic gases including radiolabelled (mainly tritiated) methane and its heavier homologous ethane, propane and butane.

#### 7.2.1. Inorganic gases

Tritiated hydrogen, HT, was suggested already in 1955<sup>31</sup> for interwell field use. Since then it has been applied as one of the most trusted tracers in interwell investigations. A number of successful tests seem to confirm its applicability<sup>35-38,40,43</sup>. However, a modification to this conclusion is given below.

The noble gas  $^{85}\text{Kr}$  ( $t_{1/2} = 10.76$  y) was proposed simultaneously<sup>31</sup> and has later become a working horse in interwell gas tracing<sup>32,33,35-40,43,45</sup>.

Also the noble gas  $^{133}\text{Xe}$  ( $t_{1/2} = 5.25$  d) has been applied to map the degree of fracturing in smaller reservoirs<sup>32</sup>. In larger reservoirs  $^{133}\text{Xe}$  is far too short-lived unless, maybe, for detection of well-to-well oriented large (10-7) fractures and cracks responsible for rapid gas break-through within the first month after injection. The longest-lived radioactive Xe-isotope,  $^{127}\text{Xe}$  ( $t_{1/2} = 36.4$  d) may replace  $^{133}\text{Xe}$  in larger reservoirs. Yet, reservoir application of  $^{127}\text{Xe}$  has not been reported.

### 7.2.1.1. Small-scale behavior

The interpretation of the results from most of the tracer tests including one or more of the tracers mentioned in sections 7.2.1 above, and also those mentioned in section 7.2.2. below, have not to any substantial degree included a consideration of the tracer behavior on the microlevel. Keywords are sorption, partitioning, chemical reaction and isotopic exchange. The main reason is that these parameters have not been studied in any detail previously. Accordingly, observed phenomena like low tracer recovery, gas break-through times and, maybe, even assessment of sweep volumes have been wrongly interpreted. Therefore, a detailed study of the basic tracer interactions is imperative.

The stability and reactions of HT has been tested in controlled laboratory experiments in the authors laboratory<sup>99</sup>. HT was contacted with various media like steel surfaces, carbonate rock material, oil and water at reservoir temperature (100 °C) and pressure (270 bar). A significant sorption ( $\approx 30\%$ ) to the steel surfaces was noticed, probably through hydride formation. No serious reactions with rock or oil was measured. With water, however, a substantial isotopic exchange (10-20 %) took place, thus producing tritiated water HTO. Accordingly, care should be exercised in application of HT: 1. Steel surfaces may be contaminated on the injection side. Contamination may be avoided by application of inactive hydrogen carrier gas. On the production side the same reactions may take place, though probably to a smaller degree due to scale coverage of internal tubing surfaces. 2. HT should not be applied together with HTO in the same reservoir if an overlap of the flow field may be expected.

This detailed information on the microscale behavior of HT was considered so serious that HT could not be recommended for a planned gas tracer injection in the Ekofisk field. These tracer pulse degradation reactions have certainly been effective also in previous field tests with HT without having been recognized and corrected for.

<sup>85</sup>Kr and the other noble gases are not prone to serious chemical reactions or degradation in the reservoir. Their dynamical movement in a reservoir is determined by the partitioning between the fluid phases present, particularly between the gas and the oil phases (see below).

The dynamic movement of <sup>85</sup>Kr relative to CH<sub>3</sub>T has been examined in the author's laboratory with the method described in ref.11 and briefly summarized in chapter 7.2.2.1. below. A slight delay only was noticed<sup>12)</sup>.

### 7.2.1.2. Requirements for field applications

The tritium half-life of 12.32 y is ideal for use in large reservoirs where a test may last for several years.

Even though there are serious limitations in the use of HT, it may certainly be applied for certain simpler purposes. The applicability of HT should be examined for each actual situation. The reported amount of HT applied per injection has normally been in the range 370 - 2775 GBq (10 - 75 Ci).

The analysis of HT may be carried out by direct counting in sealed gas proportional counters equipped with an active anticoincidence shield in order to reduce the background, especially from cosmic rays and other external radiation. Detection limits of the order of  $10^2 - 10^3$  Bq/l may be obtained depending on the quality and the size of the proportional counter. Another method is based on extraction of HT by sequential fractionation of the sampled gas, conversion of HT + carrier  $H_2$  to HTO and counting by low-background liquid scintillation beta spectroscopy. The latter method gives a lower detection limit of the order of  $10^3$  Bq/l provided a full "normal" gas sample volume of 0.5 l at 70 bar is used for the preparation of the counting sample.

$^{85}Kr$  is the only radioactive noble gas isotope with longstanding and extensive application in oil reservoirs. Amounts injected range normally from 370 GBq (10 Ci) to 2775 GBq (75 Ci).

The analytical sensitivity is limited by the background count rate of  $\approx 1.5$  cpm (Quantulus 1220) corresponding to 0.04 Bq in the sample. If  $^{85}Kr$  is separated from the full volume of a "normal" gas sample size of 0.5 l at 70 bar with 50 % separation yield, the detection limit is in the order of  $2 \cdot 10^{-4}$  Bq/l gas (at NTP).

### 7.2.2. Organic gases

The extensive field use of organic radioactive gas tracers has mainly been restricted to the tritiated molecules methane ( $CH_3T$ )<sup>31,34-36,38-40,42-45</sup>, ethane ( $C_2H_5T$ )<sup>15,34,39,40,42-45</sup>, propane ( $C_3H_7T$ )<sup>34,39,40,44</sup> and butane ( $C_4H_9T$ )<sup>34,42,44,45</sup>. These gases may be labelled also in one of the carbon positions with  $^{14}C$ , thus giving rise to a parallel series of radiotracers. They are, however, considerably more expensive than their tritiated versions. This has so far hampered their use in the field.

The inactive counterparts of the mentioned tracers are components in injected natural gas. Accordingly, the individual tracers will ideally follow their correspondingly inactive gas components ideally along the gas flow volume.

#### *7.2.2.1. Small-scale behavior*

Systematic and extensive studies of the relative dynamic movement of the various radiolabelled organic tracers as a function of parameters like temperature, pressure, type of rock material and oil and water saturation, including measurements of partition coefficients, have not been reported until recently<sup>11,12</sup>. In the author's laboratory a special experimental equipment has been constructed, built and dedicated to measurements of this type<sup>11</sup>. The equipment is based on a temperaturecontrolled column of variable length (6 - 24 m) which may be filled with a porous rock material. The rock material may vary in type and composition. It may be dry or prepared

to residual oil or residual water saturation or both. The gas flow rate through the medium and all the parameters mentioned above are experimental variables.

Tritiated methane,  $\text{CH}_3\text{T}$ , has been defined as the standard reference gas tracer to which all other gas tracer candidates are compared.

The tracer candidates are injected on the column together with  $\text{CH}_3\text{T}$  as a small-volume slug, and the production profiles are recorded as a function of the eluted gas volume in units of pore volume PV. The radioanalytical method applied on the effluent gas is liquid scintillation counting of the radioactive components after automatic sample collection directly into scintillation vials.

So far, the only radiolabelled organic molecule tested relative to  $\text{CH}_3\text{T}$  has been ethane ( $^{14}\text{CH}_3\text{CH}_3$ ). On dry silicate packing material the production profiles of methane and ethane are slightly different: The peak maxima seem to coincide, but the latter peak is somewhat broader (fig. 10 and fig. 11a.). Addition of up to 2.5 % clay has no visible effect on the dispersion profiles. With dry  $\text{CaCO}_3$  as the filling material, i.e. with extensively increased surface area, a slight delay of ethane (< 2%) is measured.

Oil on the column has a dramatic effect on the relative delay of the tracers, ethane being significantly delayed with respect to methane (see fig.12a for the case of 30% saturation of decane,  $T = 50^\circ\text{C}$  and  $p = 150$  bar). This effect is due to the difference in the tracer partitioning between oil and gas. The partition coefficient  $K = c_{\text{oil}}/c_{\text{gas}}$  for ethane decreases with increasing pressure while the one for methane seems to increase slightly, implying that the dispersion profiles for the two tracers move closer together at increased pressures (see fig.12b for the case where  $p = 250$  bar). Temperature variation in the region  $80 - 120^\circ\text{C}$  has only minor influence on  $K$ .

The main lesson is that the separation of the methane and ethane peaks is sensitive to the residual oil (or rather contactable oil) saturation, SOR. Accordingly, SOR may possibly be determined in interwell tracer tests where methane and ethane are injected together provided the values and variations in  $K$  is known as a function of the pertinent reservoir parameters.

Similar experiments should be performed for radiolabelled propane, butane and other possible hydrocarbon gas tracer candidates.

#### 7.2.2.2. Tracer molecule degradation

There are two physical degradation mechanisms possible: 1. Entropy-driven isotopic exchange where the radioactive atom is exchanged with a corresponding inactive atom from molecules in the surroundings, and 2. radiation-induced self-degradation or radiolysis where the radioactive label ends up attached to molecules in the surroundings.

We have examined the significance of such degradation for the gas tracer molecules  $\text{CH}_3\text{T}$ ,  $^{14}\text{CH}_4$ ,  $\text{C}_7\text{H}_5\text{T}$  and  $^{14}\text{CH}_3\text{CH}_3$  in contact with decane or water<sup>60</sup>. The experiments were designed to measure the integrated effect of the two mechanisms, hereafter called isotopic exchange reactions.

The degree of degradation is temperature dependant. The most extensive effect after 6 months contact time was found for the system  $C_2H_5T/H_2O$  at 150 °C where 3.2 % exchange of the tritium label had occurred. At 90 °C the degree of exchange was only measured to 0.06 %. In general, for normal reservoir temperatures up to 120 °C, the tracer degradation due to isotopic exchange can in most cases be neglected.

### 7.2.2.3. Field application

$CH_3T$  is the only radiolabelled organic gas tracer which has, so far, been injected in the Norwegian sector of the North Sea. An amount of 925 - 2775 GBq (25 - 75 Ci) is generally needed for one injection. The analysis is normally carried out by sampletaking followed by either gas proportional counting directly on the gas or by gas combustion in the laboratory, collection of the formed water now containing HTO and liquid scintillation counting of the water sample. The size of the water sample is restricted to  $\approx 10$  ml, corresponding to combustion of  $\approx 12$  l natural gas at NPT. Thus, the resulting detection limit is of the order of  $10^{-3}$  Bq/l gas (at NPT).

The same procedure may be applied for any of the other tritiated organic gases mentioned above when they are applied and produced individually. Then, the amount required for injection compares to the one given above for  $CH_3T$ .

If several different gas tracers are injected in a reservoir, and may be produced in mixtures, a cryogenic separation of the various components is required before combustion and water collection. In this case the ethane tracer needed for injection may be reduced by a factor of 2 and the heavier gas tracers by a further factor of 2. The detection limit decreases correspondingly.

For  $^{14}C$ -labelled gases, the  $CO_2$  after the combustion has to be collected in specially designed scintillation liquids and counted directly or synthesized via acetylene into benzene which are finally analyzed by liquid scintillation counting.

## 7.3. Non-radioactive chemical tracers

Except for a very early report on the use of helium gas in a reservoir<sup>30)</sup>, the main interest has concentrated on the poly- and perhalogenated hydrocarbons including one or more fluorine atoms in the molecule<sup>40,41,45)</sup>. The main reasons are their chemical, thermal and microbial stability, their low natural background and their high detectability by gas chromatography separation followed by electron capture detection (GC/ECD).

### 7.3.1. Polyhalogenated hydrocarbons

By polyhalogenated hydrocarbons in this chapter we mean those hydrocarbon molecules where more than one hydrogen atom is substituted by halogen atoms and, in addition, that atoms from

different halogen elements are present.

Examples of such molecules are the freons. Freon-11 ( $\text{CCl}_3\text{F}$ ), freon-12 ( $\text{CCl}_2\text{F}_2$ ) and freon-113 ( $\text{C}_2\text{Cl}_3\text{F}_3$ ) have been studied in detail in slim-tube displacement tests by Craig<sup>41</sup> in order to examine their applicability for tracing of  $\text{CO}_2$ -injections. The results were positive (though, their behavior relative to the movement of methane was not reported).

The following field injection was successful except from freon-113 (for unclear reasons). Freon-11 has also been applied in field investigations by Omoregie et al.<sup>45</sup> who claim that this molecule moves with the speed of the methane gas.

However, molecules of this kind containing chlorine have lately come into focus as strong ozone quenchers in the stratosphere. Therefore, their free application is likely to become restricted or even prohibited based on environmental protection arguments.

### 7.3.2. Perfluorinated hydrocarbons

In perfluorinated hydrocarbons all hydrogen atoms are substituted by fluorine. In general, exceptionally high stability and detectability are obtained (and they are not detrimental to the ozone layer!).

A number of perfluorinated molecules are of potential interest as gas tracers.  $\text{SF}_6$  has been used with success for many years<sup>40,41,45</sup>. Application of simple molecules like  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$  and others is certainly feasible. However, the focus is presently on cyclic molecules like perfluorodimethylcyclobutane (PDCB), perfluoromethylcyclopentane (PMCP), perfluoromethylcyclohexane (PMCH), perfluorodimethylcyclohexane (PDCH) and perfluorotrimethylcyclohexane (PTCH). Hereafter, they are commonly named PFTs. The PFTs are non-toxic, low-cost and with an exceptionally high detectability with GC/ECD.

#### *7.3.2.1. Small-scale behavior*

Detailed laboratory studies of the static and dynamic behavior of the PFTs are at present in progress at the author's laboratory. So far, the main attention has been given to PMCP and PMCH in nitrogen and natural gas surroundings. Dynamic studies have been carried out at simulated reservoir conditions as described in chapter 7.2.2.1. above, while the static equilibrium partition coefficient (K) measurements are performed in a specially constructed and dedicated experimental rig capable of simulating reservoir temperature and pressure, and where recombined reservoir oil, reservoir gas and reservoir water may be contacted. The results obtained so far are described in ref.s.11 and 12 and will be further reported in forthcoming articles.

A typical example of slim-tube tracer dispersion profiles is given in fig.10 where PMCP and PMCH has been injected together with methane and ethane radiotracers onto a dry silicate rock column. The PFT profiles are significantly broader than those for methane and ethane, but the

profile maxima seem to coincide fairly well (fig. 11a,b and c).

An example of dispersion profiles obtained in an oil-wet rock are displayed in fig. 12. The profile separation is due to the retention of the tracer molecules by the oil. The degree of retention is a function of the  $K$ -values which again depends strongly on the pressure and less strongly on the temperature, and of the degree of oil saturation. The type of carrier gas (nitrogen or methane) has only minor effect on the profiles.

As seen from fig. 12b, the PMCP behaves very similar to the ethane at reservoir conditions while PMCH has a somewhat larger retention.

As a partial conclusion, the laboratory experience so far is absolutely encouraging with respect to the reservoir applicability of PMCP and PMCH and other PFT compounds.

#### 7.3.2.2. Field application

As briefly mentioned above,  $SF_6$  has become a safe choice in gas tracing, especially where the well spacing is relatively small (< a few hundred meters) and the expected sweep volume is moderate. The reason is a moderate detection limit and no straight forward enrichment method which requires relatively large quantities (> several hundred kilos) for injection.

Application in reservoirs with larger well spacing and larger sweep volumes, like in several North Sea reservoirs, is, however, not excluded because of the reasonable material cost.

The very first field injection of the PFTs PMCP, PMCH and PDCH (50 g of each) was carried out by our group at the Ekofisk field (limestone rock) in 1986 before any detailed laboratory examinations has started. Analysis of the collected gas samples was carried out by Senum et al.<sup>61)</sup>, and traces of the PFTs were recorded.

Very recently (1991), 5 kg of PMCP has been injected in another North Sea reservoir (sandstone rock). Tracer breakthrough was recorded one month later with overwhelming analytical response. This is the very first demonstration of the applicability of the perfluorinated hydrocarbons as tracers for injected gas in oil and gas reservoirs.

Both oil and gas samples are collected at the test separator position with pressures in the range 50-70 bar and a temperature somewhat lower than the reservoir temperature. At these conditions the highest tracer concentration is found in the oil phase (the  $K$ -value increases with reduction in pressure). Gas samples of 0.5-1 l are treated by combustion of the hydrocarbon content in a mixture with oxygen over a  $V_2O_5$  catalyst column kept at  $\approx 400$  °C while the PFTs are unaffected. The PFTs are subsequently collected on a 10 ml charcoal (Ambersorb) column followed by thermal desorption and recollection on a 0.5 ml Ambersorb column catcher (CATS) in order to clean the sample further. In the final thermal desorption of the CATS, the PFTs are swept directly into a GC/ECD system for analysis.

The treatment of the 0.5 l oil sample start with pressure release followed by nitrogen extraction of the PFTs into the gas phase. The subsequent procedure follows closely that described above

for gas samples. With this relatively rude method detection limits of  $10^{-12}$  l/l are routinely achieved. A further factor of  $10^2$  is obtainable with optimized procedures.

The practical application of PFTs for reservoir description is only in the very beginning. Based on all good signs from extensive laboratory experiments and the modest experiences from field tests so far, it is likely to believe that a significant expansion in their use will occur.

#### 7.4. Gas tracers,- summary and recommendations

Table 2 concentrates the present state of knowledge about oil reservoir gas tracers and gives a few guidelines and recommendations for use.

Some of the tracer molecules listed have not been applied (not reported) in actual interwell field tests. These are  $^{13}\text{CD}_4$ ,  $^{127}\text{Xe}$ ,  $^{14}\text{CO}_2$  and the  $^{14}\text{C}$ -labelled hydrocarbons. However, the chemistry for the carbon-containing tracers is not significantly different from the tritiated or the non-labelled versions of the respective molecules, nor are their physical interactions. The same is true for the xenon isotopes. Their dynamic interactions are therefore considered largely known, and, although some differences may be expected in diffusion-controlled interactions, no surprises are expected in their gross rate of movement in reservoirs.

## 8. CONCLUSION AND FUTURE DIRECTION OF DEVELOPMENT

Although the tracer technique in reservoir description is an aging idea, its rate of development into a unique and useful instrument has not been particularly impressive. In the later years, however, both dedicated laboratory experiments and well planned and executed field tests have added positively to the knowledge of tracer behavior under extreme conditions like those encountered in oil reservoirs. Hence, the present status is a collection of well examined tracers for water and gas movement as given in tables 1 and 2.

However, the existing limited collection does not offer sufficient freedom, versatility and capacity to the user, especially for the use in complex reservoirs with many wells. Hence, there is a *continued strong need* to enlarge the collection of well-characterized water and gas tracers.

The present development concentrates on various tasks:

1. Ideal or near-ideal tracers for the purposes listed in points a-d in chapter 3.
2. Water/oil and gas/oil partitioning tracers for possible interwell determination of residual oil (or rather watercontactable remaining oil) saturation. Crucial here is the determination of K-values as a function of changing reservoir parameters like pressure, temperature, water pH and salinity, oil and gas composition etc.

A field test with positive conclusion has already been conducted using phenol and



ortho-cresol as partitioning tracers<sup>62</sup>).

3. Reversibly rock-sorbing tracers for determination of the average interwell ion exchange capacity which is mainly associated with the clay content. This parameter is of interest in tertiary oil recovery when polar or ionic surfactants are planned used.
4. Water/oil partitioning tracers for signaling waterfront approach before water breakthrough. It is recently demonstrated theoretically that such measurements are feasible<sup>63</sup>.
5. Gas/oil partitioning tracers for signaling gas coning before gas breakthrough.

The new tracers are sought both among the radioactively labelled molecules, the non-radioactive molecules (in particular the poly- and perfluorinated chemicals) and the molecules labelled with stable isotopes with low natural abundances<sup>64</sup>.

In addition to the tracer development itself, attention will be concentrated on their application and interpretation, for instance in improved description and quantification of permeability inhomogeneities, barriers to flow, spatial distributions of residual oil and clay concentrations, interwell measurement of the degree of imbibition and of the changing imbibition potential, measurement of the relative volumes of fractures and non-cracked rock and possibly also quantification of reservoir rock wettability.

In addition to correct formulation of tracer cocktails, a prerequisite for fruitful and advanced tracer applications in the mentioned areas is the existence of highly developed tracer simulation models. Here, the experimental and theoretical development should go hand-in-hand. In the author's institution these activities are well coordinated of benefit to a more efficient development of both branches.

Before any general recommendations can be made on the use of new tracer methods, the results of both the experimental and theoretical development should be jointly tested in real reservoir experiments where several tracers are injected together in a cocktail in order to facilitate direct comparison of the recorded tracer production profiles. The test reservoir should preferably be well characterized with respect to mineralogy, stratifications and saturations.

At present, there is a growing awareness among potential users of the interesting inherent possibilities in the tracer technique, and also a growing impatience towards a more rapid examination of these possibilities. As a result, several research groups are working seriously, and on a highly sophisticated level, both with support from single companies and institutions but also on programs which are jointly supported and financed by several companies because of acknowledged common interests in this matter.

Accordingly, the signs are positive for a relatively near future with well developed tracer techniques as an indispensable and inevitable instrument, a must, in reservoir description.

## References

1. J.W. Watkins and E.S. Mardock, "Use of Radioactive Iodine as a Tracer in Water-Flooding Operations", J. Petr. Tech. 6(9) (1954) 117.
2. R.J. Heemstra, J. Wade Watkins and F.E. Armstrong, "Laboratory Evaluations of Nine Water Tracers", Nucleonics (Jan. 1961) 92.
3. R.A. Greenkom, "Experimental Study of Waterflood Tracers", J. Petr. Tech. (Jan.1962) 87.
4. I. Durusu, "Laboratory Investigation of a Suitable Waterflood Tracer for the Bulgurdag Field and a Design of a Tracer Field", SPE 4826, 1974.
5. C.S.H. Chen, Y. Luh and K.D. Schmitt, "Fluorine-Containing Tracers for Subterranean Petroleum and Mineral Containing Formations", U.S. Patent 4.303.411, 1981.
6. I.A. Hundere and O.B. Michelsen, "Laboratory experiments with Potential Radioactive Tracers for Front Tracking of Injected Sea Water in the Gullfaks Field" (in Norwegian), IFE/KR/F-86/104, 1986 (conf.)
7. K.Garder and I.A. Hundere, "SPOR-OPT: Tracer methods for Reservoir Studies", IFE/KR/F-88/098, 1988.
8. K. Garder, B. Antonsen, I.A. Hundere and J. Sagen, "SPOR-OPT: Tracer Testing for Improved Reservoir Description" (partly in Norwegian), IFE/KR/F-89/034, 1989.
9. T. Bjørnstad, "Application of Radioactive Tracers for Improved Oil Recovery - Annual Report 1988", IFE/KR/F-89/054, 1989 (conf.).
10. T. Bjørnstad, "Application of Radioactive Tracers for Improved Oil Recovery - Annual Report 1989", IFE/KR/F-90/003, 1990 (conf.).
11. Ø. Dugstad, T. Bjørnstad and I.A. Hundere, "Construction of a Slim-Tube Equipment for Gas-Tracer Evaluation at Simulated Reservoir Conditions", in manuscript, to be published 1991.
12. Ø. Dugstad, T. Bjørnstad and I.A. Hundere, "Measurements of Gas Tracer Retention Under Simulated Reservoir Conditions", in manuscript, to be published at the "3rd Conference and Technical Exhibition EAPG", Florence, 26-30 May, 1991.
13. F.A. Alekseev, V.N. Soyfer, V.A. Filonov and Ya.B. Finkel'shteyn, "Use of the Tritium Isotope of Hydrogen in Development of Oil Fields", *Geologija Nefti (Petroleum Geology)* 2 (1958) 1039.
14. E.L. Burwell, "Multiple Tracers establish Waterflood Flow Behavior", Oil and Gas J. (Nov.1966) 76.
15. O.R. Wagner, L.E. Baker and G.R. Scott, "The Design and Implementation of Multiple Tracer Programs for Multifluid, Multiwell Injection Projects", SPE 5125, 1974.
16. H.E. Gilland and F.R. Conley, "Pilot Flood Mobilizes Residual Oil", Oil and Gas J. (Jan.19,1976) 46.
17. O.R. Wagner, "The Use of Tracers in Diagnosing Interwell Reservoir Heterogeneities - Field Results", J. Petr. Tech. (Nov. 1977) 1410.
18. L.K. Strange and A.W. Talash, "Analysis of Salem Low-Tension Waterflood Test", J. Petr. Tech., Nov., 1380(1977).

19. R.H. Widmyer, A. Satter, G.D. Frazier and R.H. Graves, "Low-Tension Waterflood Pilot at the Salem Unit, Marion County, Illinois - Part 2: Performance Evaluation", *J. Petr. Tech.* (Aug. 1977) 933.
20. J.A. D'Hooge, C.Q. Sheely and B.J. Williams, "Interwell Radioactive Tracers - An Effective Reservoir Evaluation Tool: West Sumatra Field Results", *SPE* 8434, 1979.
21. J.C. Trantham, C.B. Threlkeld and H.L. Patterson, "Reservoir Description for a Surfactant/Polymer Pilot in a Fractured, Oil-Wet Reservoir - North Burbank Unit Tract 93", *J. Petr. Tech.* (Sept. 1980) 1647.
22. J.D. Griffith and L.G. Cyca, "Performance of South Swan Hills Miscible Flood", *J. Petr. Tech.* (July, 1981) 1319.
23. K. Ohno and T. Nanba, "Analysis of an Interwell Tracer Test in a Depleted Heavy Oil Reservoir", *SPE* 13672, 1985.
24. P.J. Briggs, "The Use of Tracers in Reservoir Management", *BPX Petroleum/Production Engineering Conference 1985*, Paper IIB, January 1985.
25. R.P. Heisler, "Interpretation of Radioactive Tracer Results in a Steamdrive Project", *SPE* 15092, 1986.
26. T. Stone, E. Perkins and T. Schmidt, "Tracers in Analysis of Steamfloods", Paper No 20 presented at the "Third Technical Meeting of the South Saskatchewan Section, the Petroleum Society of CIM", Regina, Sept. 25-27, 1989.
27. A.M. Al-Dolaيمي, D. Berta, M.J. Dempsey and P.J. Smith, "Evaluating Tracer Response of Waterflood Five-Spot Pilot: Dukhan Field Qatar", *SPE* 17989, 1989.
28. O. Skilbrei, L.D. Hallenbeck and J.E. Sylte, "Comparison and Analysis of Radioactive Tracer injection Response with Chemical Water Analysis into the Ekofisk Formation Pilot Waterflood", *SPE* 20776, 1990.
29. S.A. Rogde, "Interpretation of Radioactive Tracer Observations in the Gullfaks Field", Paper presented at the "International Energy Agency Symposium on Reservoir Monitoring", Paris, October 8, 1990.
30. E.M. Frost, Jr., "Helium Tracer Studies in the Elk Hills, Calif., Fields", *Bureau of Mines Research Report BM-RI-3897*, 1946.
31. H.J. Welge, "Super Sleuths Trace Flow of Injected Gas", *Oil and Gas J.* 54 (1955) 77.
32. F.E. Armstrong, W.D. Howell and J. Wade Watkins, "Radioactive Inert Gases as Tracers for Petroleum Reservoir Studies", *Bureau of Mines Report of Investigations BM-RI-5733*, 1961.
33. E.L. Burwell and W.D. Howell, "Krypton-85 Tracer Aids Evaluation of Underground Combustion Oil Recovery Tests", *Prod. Mon.* 29(1) (1965) 21.
34. M. Gondouin, J.J. Comar and P. Thiebierge, "Etude du Champ Petroliere d'Hassi Messaoud par Injection de Methane, Ethane, Propane et Butane Trities", *Proc. Symp. Radioisot. Tracers in Industry and Geophys. Intern. Atom. Energy Agency, Vienna, 1967*, pp. 161.
35. T.G. Calhoun and R.M. Title, "Use of Radioactive Isotopes in Gas Injection", *SPE* 2277, 1968.
36. T.G. Calhoun and G.T. Hurford, "Case History of Radioactive Tracers and Techniques in Fairway Field", *J. Petr. Tech.* (Oct. 1970) 1217.
37. G.E. Tinker, "Gas Injection with Radioactive Tracers to Determine Reservoir Continuity - East Coalinga Field, California", *J. Petr. Tech.* (Nov. 1973) 1251.

38. J.A. Davis, R.K. Blair and O.R. Wagner, "Monitoring and Control Program for a Large Scale Miscible Flood", SPE 6097, 1976.
39. K.A. Rupp, W.C. Nelson, L.D. Christian, K.A. Zimmerman, B.E. Metz and J.W. Styler, "Design and Implementation of a Miscible Water-Alternating-Gas Flood at Prudhoe Bay", SPE 13272, 1984.
40. E.P. Langston and J.A. Shirer, "Performance of Jay/LEC Fields Unit Under Mature Waterflood and Early Tertiary Operations", J. Petr. Tech. (Feb. 1985) 261.
41. F.F. Craig, "Field Use of Halogen Compounds to Trace Injected CO<sub>2</sub>", SPE 14309, 1985.
42. F.J. McIntyre and G. Polkowski, "Radioactive Tracer Application to Monitoring Solvent Spreading in the Rainbow Keg River B Pool Vertical Hydrocarbon Miscible Flood", SPE 14440, 1985.
43. C.J. Mayne R.W. Pendleton, "Fordoche: An Enhanced Oil Recovery Project Utilizing High Pressure Methane and Nitrogen Injection", SPE 14058, 1986.
44. S. Asgarpour, A.L. Crawley and S.J. Springer, "Performance Evaluation and Reservoir Management of a Tertiary Miscible Flood in the Fenn-Big Valley South Lake D-2A Pool", Paper No. 87-38-07 presented at "The 38th Annual Technical Meeting of the Petroleum Society of CIM", Calgary, June 7-10, 1987.
45. Z.S. Omoregie, S.L. Vasicek, G.R. Jackson and L.A. Martinson, "Monitoring the Mitsue Hydrocarbon Miscible Flood,- Program Design, Implementation and Preliminary Results", Paper No. 87-38-06 presented at "The 38th Annual Technical Meeting of the Petroleum Society of CIM", Calgary, June 7-10, 1987.
46. R.A. Beier and C.Q. Sheely, "Tracer Survey to Identify Channels for Remedial Work Prior to CO<sub>2</sub> Injection at the MCA Unit, New Mexico", SPE/DOE 17371, 1988.
47. J.H. Randall, T.R. Schultz and S.N. Davis, "Suitability of Fluorocarbons as Tracers in Ground Water Resources Evaluation", Project Completion Report OWRT A-063-ARIZ, Arizona University, Tucson, 1977.
48. S.N. Davis, D.J. Campbell, H.W. Bentley and T.J. Flynn, "An Introduction to Ground Water Tracers", Univ. of Arizona, EPA/600/2-85/022, 1985.
49. S.L. Kerrin, "Perfluorocarbons as Hydrological Tracers", NSF/CPE-81015, Washington, DC, 1981.
50. S. Barr, W.E. Clements and P.R. Guthals, "Atmospheric Tracer Workshop", Proc. from "Workshop on Atmospheric Tracers", Report No. LA-10301-C, Santa Fe, New Mexico, 21 May, 1984.
51. R.N. Dietz, "Perfluorocarbon Tracer Technology", BNL-38847, 1986.
52. "Isotope Techniques in the Hydrogeological Assessment of Potential Sites for the Disposal of High-Level Radioactive Wastes", Technical Report Series No. 228, IAEA, Vienna, 1983.
53. V.I. Ferronsky and V.A. Polyakov, "Environmental Isotopes in the Hydrosphere", John Wiley & Sons, Ltd., 1982, p.255.
54. T. Bjørnstad, E. Brendsdal, O.B. Michelsen and S.A. Rogde, "Analysis of radiolabelled thiocyanate tracer in oil field brines", Nucl. Instr. Meth. in Phys. Res. A299 (1990) 629.
55. T. Bjørnstad, Institutt for energiteknikk, 1989, unpublished results.
56. G. Haberstock, J. Heinzl, G. Korschinek, H. Morinaga, E. Nolte, U. Ratzinger, K. Kato and M. Wolf, "Accelerator Mass Spectrometry with Heavy Ions", Nucl. Instr. Meth. in Phys. Res. B17 (1986) 385.

57. T. Bjørnstad and S.A. Rogde, "An Improved Gammasspectrometric Method for Trace Analysis of  $^{22}\text{Na}$ ", Nucl. Instr. Meth. in Phys. Res. A299 (1990) 634.
58. G.A. Cowan, D.G. Ott, A. Turkevich, L. Machta, G.J. Ferber and N.R. Daly, "Heavy Methanes as Atmospheric Tracers", LA-UR-75-1988, 1975.
59. J.B. Dahl and I.A. Hundere, "The Applicability of Tritiated Hydrogen as a Gas Tracer in the Ekofisk Field", IFE/KR/F-87/004, 1987 (conf.)
60. Ø. Dugstad and T. Bjørnstad, "Isotopic Exchange of Tritium and  $^{14}\text{C}$  in a Gas/Liquid system", in manuscript for publication, 1991.
61. G.I. Senum, R.N. Dietz, T.W. D'Ottavio, R.W. Goodrich, E.A. Cote and D.J. Spandau, "A Perfluorocarbon Tracer Transport and Dispersion Experiment in the North Sea Ekofisk Oil Reservoir", Informal Report BNL-43811, Dec. 1989.
62. E. Causin, J. Rochon and D. Marzorati, "Field Measurement of Remaining Oil Saturation", SPE/DOE 20260, 1990.
63. B. Antonsen, T. Johansen and J. Sagen, "The Use of Partitioning Tracers as a Tool for Determination of Breakthrough Times. A Theoretical Study", Proc. SPOR-Seminar 1990, Norwegian Petroleum Directorate, Stavanger, 3-4 October 1990, p.112.
64. D.R. Janecky and W.D. Spall, "New Tracer Technology for Geochemical Tomography", Proc. SPE/Univ. of Houston Conf. "Emerging Technologies Conference", University of Houston, Houston, Texas, July 5-7, 1990, p.281.

TABLE 1. Interwell water tracers.

TRACER	HALF-LIFE	TEST DURATION <1.5 y	TEST DURATION >1.5 y	RESERVOIR TYPE		RADIATION TYPE	APPROX. DETECT. LIMIT <sup>h)</sup>	APPROX. AMOUNT NEEDED <sup>k)</sup> GBq(Ci)	APPROX. TRACER COST <sup>l)</sup> NOK (* 10 <sup>3</sup> )	ANA- LYTICAL METHOD
				SAND- STONE	LIME- STONE					
A. ISOTOPIC RATIOS										
D/H	-	Y <sup>n)</sup>	Y	Y	Y	-	S <sub>8D</sub> = 0.5 ‰ <sup>i)</sup>	-	-	MS <sup>m)</sup>
<sup>87</sup> Sr/ <sup>86</sup> Sr	-	Y	Y	(Y)	(Y)	-	S <sub>R</sub> = 2 * 10 <sup>-5</sup> <sup>j)</sup>	-	-	MS
B. RADIOACTIVE SPECIES										
HTO	12.32 y	Y	Y	Y	Y	β <sup>d)</sup>	1.5 - 2 Bq/l	3700 (100)	30	LSC <sup>n)</sup>
<sup>22</sup> Na <sup>+</sup>	2.6 y	Y	Y	Y	P	β <sup>+e)</sup> , γ <sup>o)</sup>	0.1 Bq/l	18.5 (0.5)	500	LSC, GAM <sup>o)</sup>
<sup>36</sup> Cl <sup>-</sup>	3 * 10 <sup>5</sup> y	Y	Y	Y	Y	β <sup>-</sup>	<10 <sup>-5</sup> at/at	1.85 (0.05) (~ 2 * 10 <sup>22</sup> atoms)	100	AMS <sup>p)</sup>
<sup>125</sup> I <sup>-</sup>	60 d	Y	N <sup>b)</sup>	Y	Y(P)	ε <sup>q)</sup> , γ	<0.05 Bq/l	37 (1)	150	LSC, GAM
<sup>14</sup> CN <sup>-</sup>	5730 y	Y	Y	Y	P	β <sup>-</sup>	0.005 Bq/l	37 (1)	200	LSC
<sup>35</sup> SCN <sup>-</sup>	87 d	Y	N	Y	P	β <sup>-</sup>	0.005 Bq/l	37 (1)	200	LSC
<sup>35</sup> SO <sub>4</sub> <sup>2-</sup>	87 d	Y	N	Y	P	β <sup>-</sup>	<0.05 Bq/l	37 (1)	-	LSC

Probable tracers, but awaiting experimental clarification:

$^{129}\text{I}^-$	$1.6 \times 10^7 \text{ y}$	Y	Y	Y	Y(P)	$\beta^-$ , $\gamma$	$<10^{-15} \text{ at/at}$	$0.03 (8 \times 10^{-4})$ $(2 \times 10^{22} \text{ atoms})$	150	AMS
$^{56}\text{Co}(\text{CN})_6^{3-}$	78 d	Y	Y	P <sup>b)</sup>	P	$\epsilon$ , $\beta^+$ , $\gamma$	$\sim 0.01 \text{ Bq/l}$	18-37 (0.5-1)	-	LSC, GAM
$^{57}\text{Co}(\text{CN})_6^{3-}$	270 d	Y	Y	P	P	$\epsilon$ , $\gamma$	$\sim 0.01 \text{ Bq/l}$	18-37 (0.5-1)	-	LSC, GAM
$^{58}\text{Co}(\text{CN})_6^{3-}$	71 d	Y	N	P	P	$\epsilon$ , $\beta^+$ , $\gamma$	$\sim 0.01 \text{ Bq/l}$	18-37 (0.5-1)	-	LSC, GAM
$^{60}\text{Co}(\text{CN})_6^{3-}$	5.2 d	Y	Y	P	P	$\beta^-$ , $\gamma$	$\sim 0.01 \text{ Bq/l}$	18-37 (0.5-1)	-	LSC, GAM
$\text{Co}(\text{CN})_5$ $(^{14}\text{CN})^{3-}$	5730 y	Y	Y	P	P	$\beta^-$	$\sim 0.01 \text{ Bq/l}$	18-37 (0.5-1)	-	LSC

C. NON-RADIOACTIVE SPECIES

Fluorescein	-	Y	?	P(SR)	P(SR)	-	-	$> 10 \text{ kg}$	-	FM <sup>a)</sup>
Methanol	-	Y	?	P(SR)	P(SR)	-	-	$> 10 \text{ m}^3$	-	GC <sup>b)</sup>
Ethanol	-	Y	?	P(SR)	P(SR)	-	-	$> 10 \text{ m}^3$	-	GC
Isopropanol	-	Y	Y	P(SR)	P(SR)	-	-	$> 10 \text{ m}^3$	-	GC
I <sup>-</sup>	-	Y	Y	Y(SR)	P(SR)	-	-	$> 1 \text{ ton}$	-	-
SCN <sup>-</sup>	-	Y	Y	Y(SR)	P(SR)	-	-	$> 1 \text{ ton}$	-	-
$\text{NO}_3^-$	-	Y	?	Y(SR)	P(SR)	-	-	$> 1 \text{ ton}$	-	CM <sup>c)</sup>
$\text{Co}(\text{CN})_6^{3-}$	-	Y	Y	P(SR)	P(SR)	-	-	$> 1 \text{ ton}$	-	HPLC <sup>d)</sup>

- a) Y = yes
- b) N = no
- c) P = probably, not sufficiently tested
- d)  $\beta^-$  = negative beta particles (negatrons)
- e)  $\beta^+$  = positive beta particles (positrons)
- f)  $\gamma$  = gamma radiation
- g)  $\epsilon$  = decay by electron capture
- h) Very approximate limits given only as a guide. Vary with complexity of the analysis.
- i) Standard deviation on  $\delta D$ . Implies a sensitivity of 0.5 - 1 % inmix of injection water into formation water (or vice versa) for normal North Sea reservoirs.
- j) Standard deviation of the ratio. The method is hardly applicable in North Sea reservoirs due to high concentration of Sr in formation water and low concentration in injection water.
- k) May vary a factor 10 from test to test.
- l) Vary with time.
- m) MS = Mass spectrometry.
- n) LSC = Liquid scintillation counting.
- o) GAM = Gamma spectroscopy.
- p) AMS = Accelerator mass spectrometry.
- q) FM = Fluorometry.
- r) GC = Gass chromatography.
- s) CM = Colorometry.
- t) HPLC = High-pressure liquid chromatography.



**TABLE 2. Interwell gas tracers.**

TRACER	HALF-LIFE	TEST DURATION		RADIATION TYPE	APPROX. DETECT. LIMIT <sup>h)</sup>	APPROX. AMOUNT RECOMMENDED <sup>k)</sup>	REL. TRACER COST	ANALYTICAL METHOD	COMMENTS
		< 1 y	> 1 y						
<b>A. "ISOTOPIC" TRACERS</b>									
<sup>13</sup> CD <sub>4</sub> + Similar Molecules	-	Y <sup>d)</sup>	Y	-	< 10 <sup>-15</sup> l/l	< 100 g	High	GC <sup>l)</sup> /MS <sup>m)</sup>	Possible, but not applied.
<b>B. RADIOACTIVE SPECIES</b>									
HT	12.32 y	Y	(Y)	β <sup>-</sup> <sup>d)</sup>	~ 10 <sup>-3</sup> Bq/l	1110 GBq (30 Ci)	Medium	Conv. <sup>o)</sup> + LSC <sup>n)</sup>	Use with caution; isotope exchange degradation.
<sup>85</sup> Kr	10.76 y	Y	Y	β <sup>-</sup> (γ)	~ 2 * 10 <sup>-4</sup> Bq/l	1110 GBq (30 Ci)	Medium	LSC	Well documented performance.
<sup>127</sup> Xe	36.4 d	Y	N <sup>b)</sup>	ε <sup>g)</sup> , γ	~ 2 * 10 <sup>-4</sup> Bq/l	1110 GBq (30 Ci)	High	LSC, GAM <sup>o)</sup>	Special cases, not previously reported.
<sup>133</sup> Xe	5.2 d	Y	N	β <sup>-</sup> , γ <sup>o)</sup>	~ 2 * 10 <sup>-4</sup> Bq/l	1110 GBq (30 Ci)	Medium	LSC, GAM	Special cases only.
<sup>14</sup> CO <sub>2</sub>	5730 y	Y	N	β <sup>-</sup>	< 5 * 10 <sup>-4</sup> Bq/l	370 GBq (10 Ci)	High/medium	Conv. + LSC	Not reported (?).
CH <sub>3</sub> T	12.32 y	Y	Y	β <sup>-</sup>	~ 10 <sup>3</sup> Bq/l	1850 GBq (50 Ci)	Medium	Conv. + LSC	Well documented use

C <sub>2</sub> H <sub>5</sub> T	12.32 y	Y	Y	β <sup>-</sup>	~ 10 <sup>3</sup> Bq/l	1850 GBq (50 Ci)	Medium	Conv. + LSC	Well documented use
C <sub>3</sub> H <sub>7</sub> T	12.32 y	Y	Y	β <sup>-</sup>	~ 10 <sup>3</sup> Bq/l	1850 GBq (50 Ci)	Medium	Conv. + LSC	Well documented use
C <sub>4</sub> H <sub>9</sub> T	12.32 y	Y	Y	β <sup>-</sup>	~ 10 <sup>3</sup> Bq/l	1850 GBq (50 Ci)	Medium	Conv. + LSC	Well documented use
<sup>14</sup> CH <sub>4</sub>	5730 y	Y	Y	β <sup>-</sup>	~ 5 * 10 <sup>-4</sup> Bq/l	370 GBq (10 Ci)	High	Conv. + LSC	Not reported
<sup>14</sup> CH <sub>3</sub> * CH <sub>3</sub>	5730 y	Y	Y	β <sup>-</sup>	~ 5 * 10 <sup>-4</sup> Bq/l	370 GBq (10 Ci)	High	Conv. + LSC	Not reported
<sup>14</sup> CH <sub>3</sub> * C <sub>2</sub> H <sub>5</sub>	5730 y	Y	Y	β <sup>-</sup>	~ 5 * 10 <sup>-4</sup> Bq/l	370 GBq (10 Ci)	High	Conv. + LSC	Not reported
<sup>14</sup> CH <sub>3</sub> * C <sub>3</sub> H <sub>7</sub>	5730 y	Y	Y	β <sup>-</sup>	~ 5 * 10 <sup>-4</sup> Bq/l	370 GBq (10 Ci)	High	Conv. + LSC	Not reported

### C. NON-RADIOACTIVE SPECIES

He	-	Y	Y	-	-	-	Low/medium	MS	Special cases
SF <sub>6</sub>	-	Y	Y	-	~ 10 <sup>-12</sup> l/l	> 10 <sup>2</sup> kg	Low	GC/ECD <sup>1)</sup>	Well documented
Freon-11	-	Y	Y	-	< 10 <sup>-9</sup> l/l	> 10 <sup>2</sup> kg	Low	GC/ECD	Probably restricted (?)
Freon-12	-	Y	Y	-	< 10 <sup>-9</sup> l/l	> 10 <sup>2</sup> kg	Low	GC/ECD	Probably restricted (?)
PMCP	-	Y	Y	-	< 10 <sup>-12</sup> l/l	5 kg	Low	GC/ECD	Promising field response.
PMCH	-	P <sup>2)</sup>	P	-	< 10 <sup>-12</sup> l/l	25 kg	Low	GC/ECD	Promising, but not sufficiently tested.

- a) As for table 1.
- b) As for table 1.
- c) As for table 1.
- d) As for table 1.
- e) Conv. = conversion of the radioactive species into another molecular form before detection.
- f) As for table 1
- g) As for table 1.
- h) As for table 1.
- i) ECD = Electron Capture Detector
- k) As for table 1
- m) As for table 1.
- n) As for table 1.
- o) As for table 1.
- r) As for table 1.

## Figure captions:

- Fig.1. Normalized dispersion profiles obtained for HTO and  $S^{14}CN^-$  tracers on a sandstone core saturated with formation water at a temperature  $T = 90\text{ }^\circ\text{C}$  and a pressure  $p = 230\text{ bar}$ .
- Fig.2. Difference in the normalized dispersion profiles from fig.1.
- Fig.3. Normalized dispersion profiles obtained for HTO and  $S^{14}CN^-$  tracers on a sandstone core which was prepared to residual oil saturation (27.4%). The remaining pore volume is filled with formation water. Other parameters were  $T = 90\text{ }^\circ\text{C}$ ,  $p = 230\text{ bar}$ .
- Fig.4. Difference in the normalized dispersion profiles from fig.3.
- Fig.5. Normalized dispersion profiles obtained for HTO and  $^{22}Na^+$  tracers on a sandstone core saturated with formation water at  $T = 90\text{ }^\circ\text{C}$  and  $p = 230\text{ bar}$ .
- Fig.6. Difference in the normalized dispersion profiles from fig.6.
- Fig.7. Normalized dispersion profiles obtained for HTO and  $^{22}Na^+$  tracers in a sandstone core prepared to residual oil saturation (27.4%). Other parameters as in the text to fig.3.
- Fig.8. Difference in the normalized dispersion profiles from fig.7.
- Fig.9. Variation in detection limit for  $^{22}Na$  as a function of the counting time with the NaI(Tl)-detector size (and the corresponding sample volume) as a parameter.
- Fig.10. Normalized dispersion profiles obtained for  $CH_3T$ ,  $^{14}CH_3CH_3$ , PMCP and PMCH on a 12 m long slim-tube filled with dry silicate mineral (Ottawa sand). Other parameters were  $T = 120\text{ }^\circ\text{C}$ ,  $p = 150\text{ bar}$  and the carrier gas is methane.
- Fig.11. The differences between the dispersion profile for methane and the dispersion profiles for ethane (a), PMCP (b) and PMCH (c), respectively.
- Fig.12. Normalized dispersion profiles obtained for  $CH_3T$ ,  $^{14}CH_3CH_3$ , PMCP and PMCH on a 12 m long slim-tube prepared to residual oil saturation (30%) and with methane as injection gas. Other parameters have been (a):  $T = 50\text{ }^\circ\text{C}$ ,  $p = 150\text{ bar}$  and (b)  $T = 50\text{ }^\circ\text{C}$  and  $p = 250\text{ bar}$ .

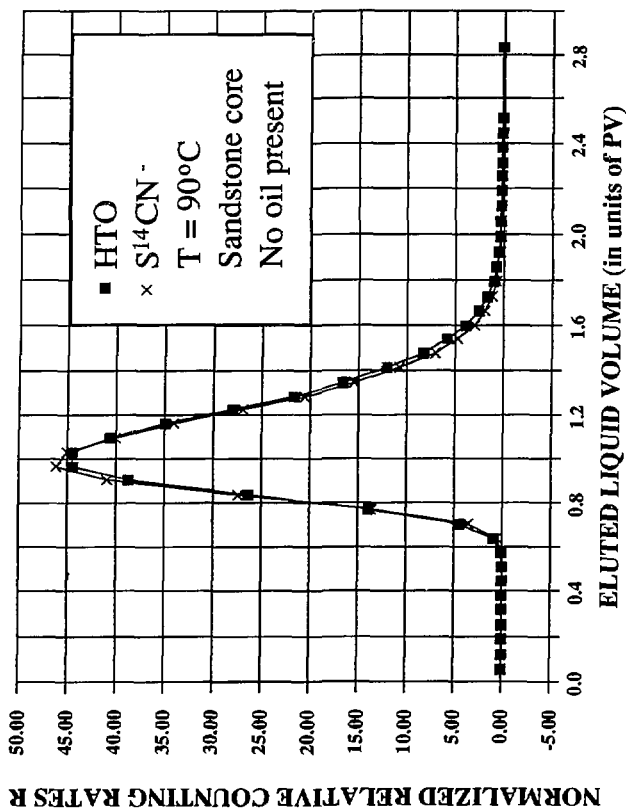


Fig.1

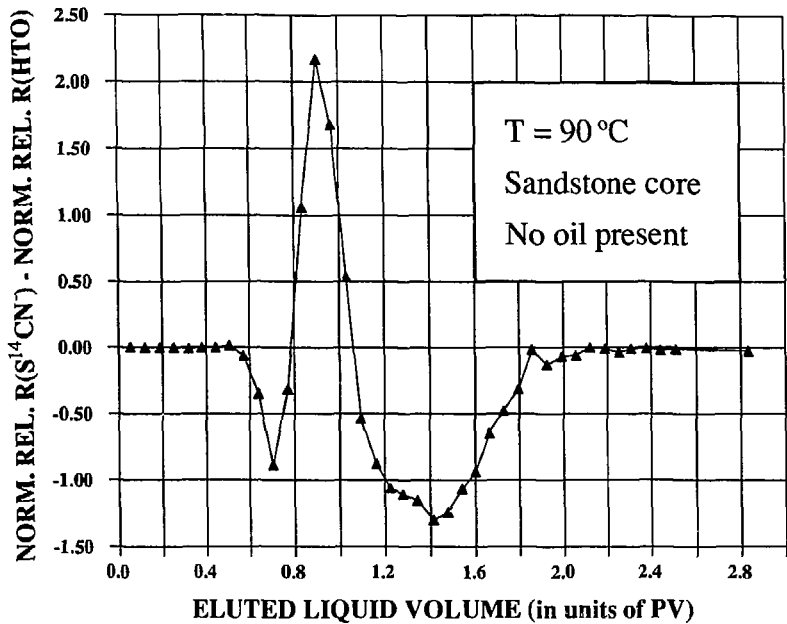


Fig. 2

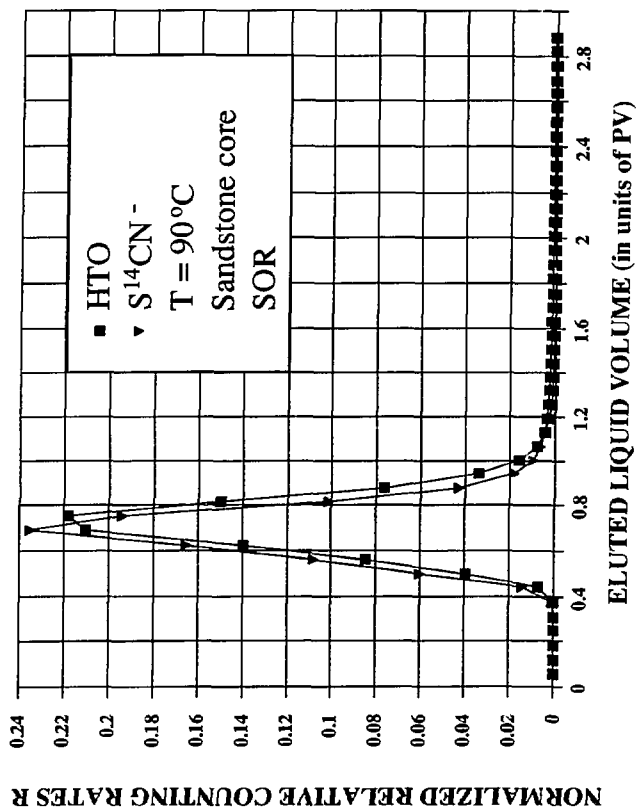


Fig.3

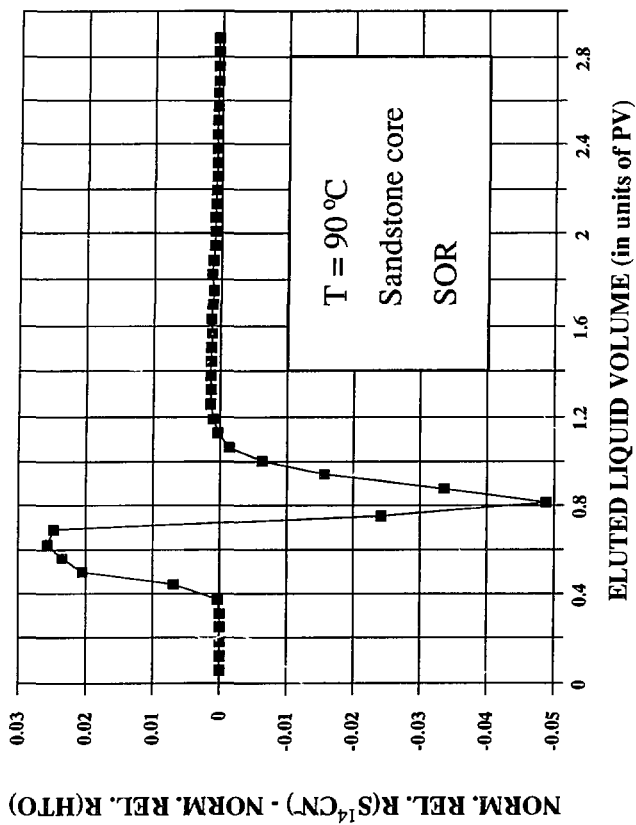


Fig.4



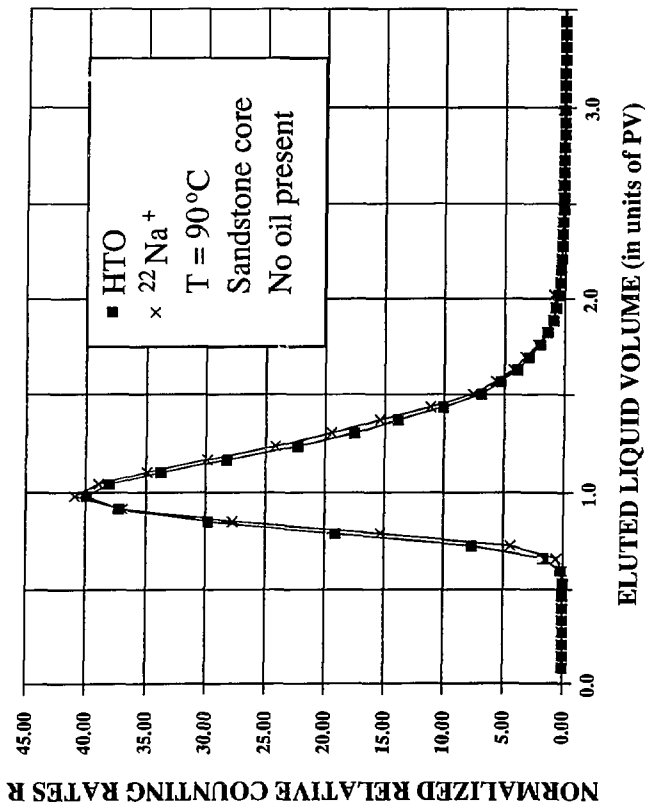


Fig.5

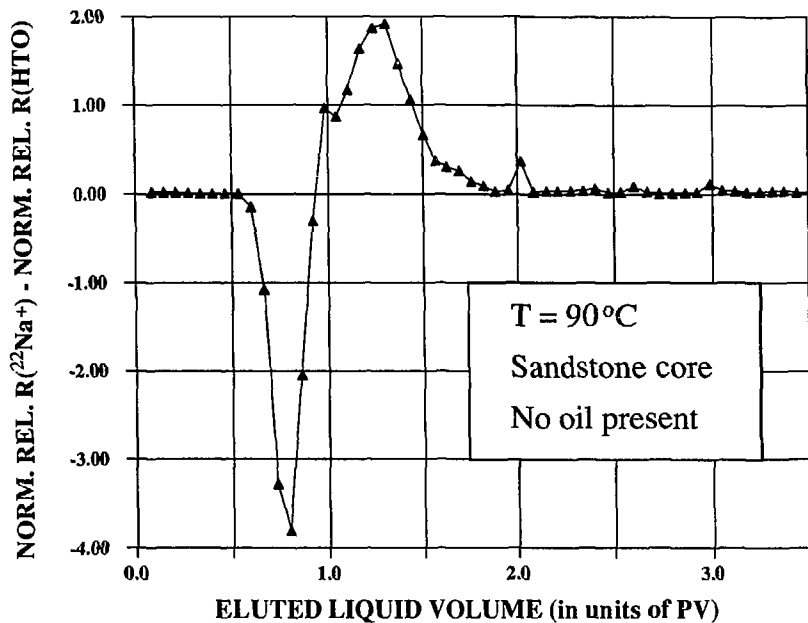


Fig.6

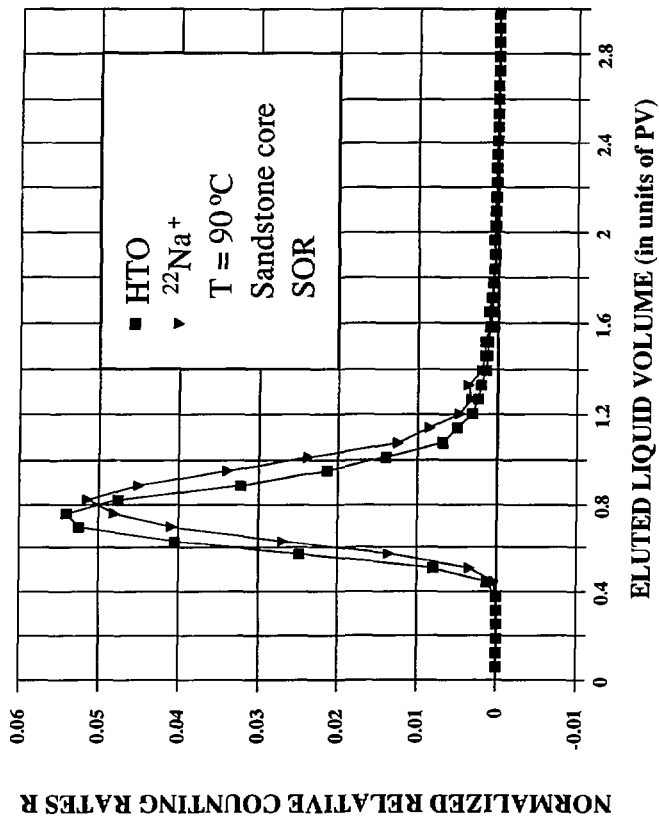


Fig.7

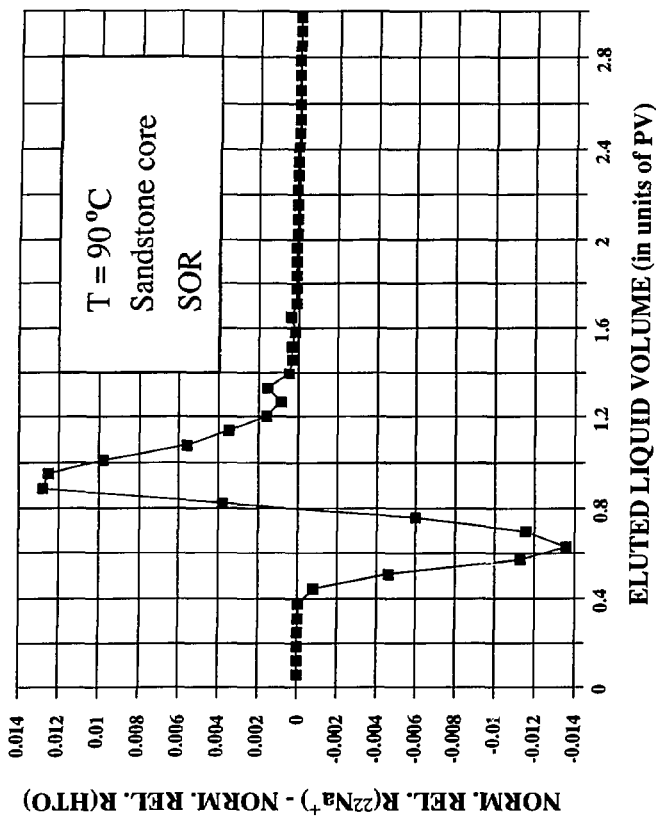
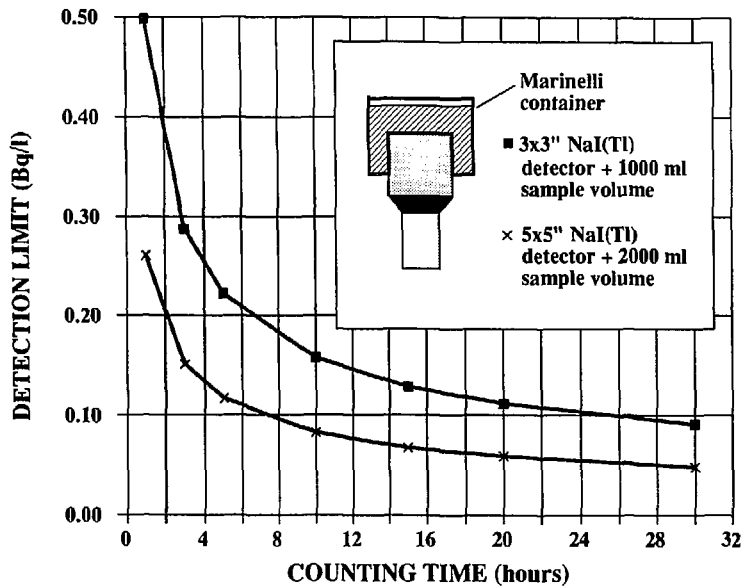


Fig.8

Fig.9



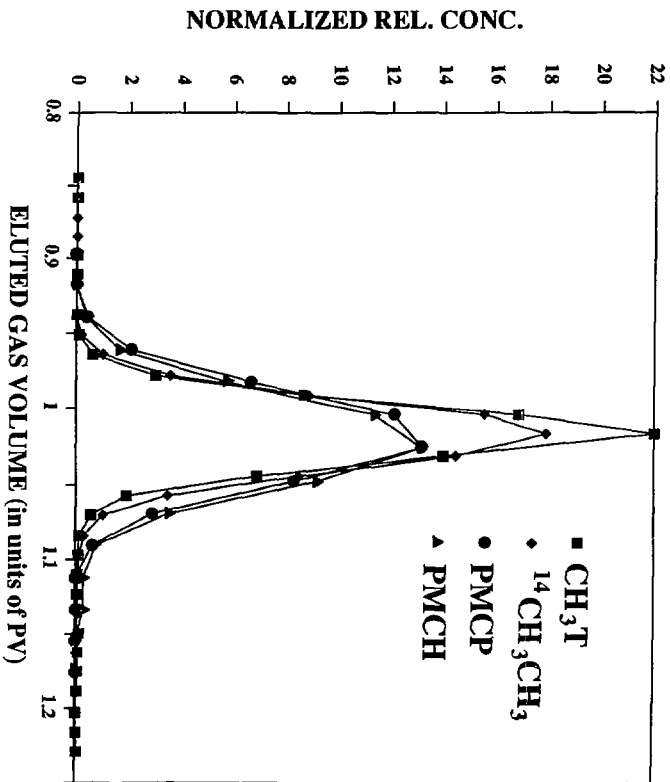


Fig.10

## DIFFERENCE IN NORMALIZED RELATIVE CONCENTRATION: TRACER - METHANE

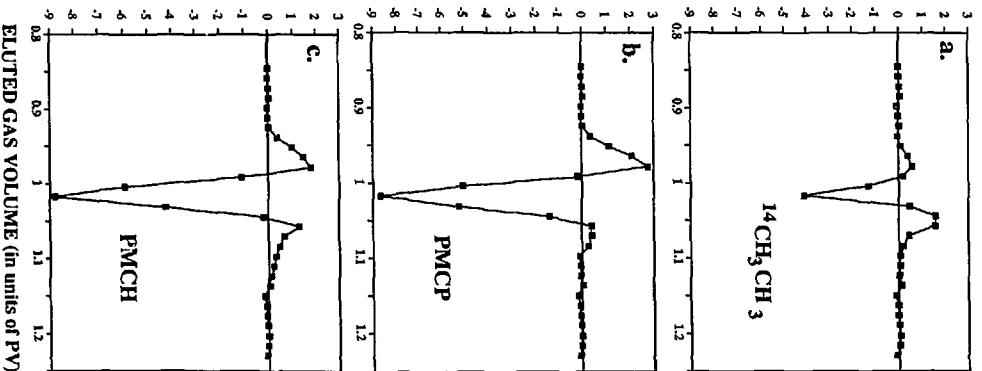


Fig. 11

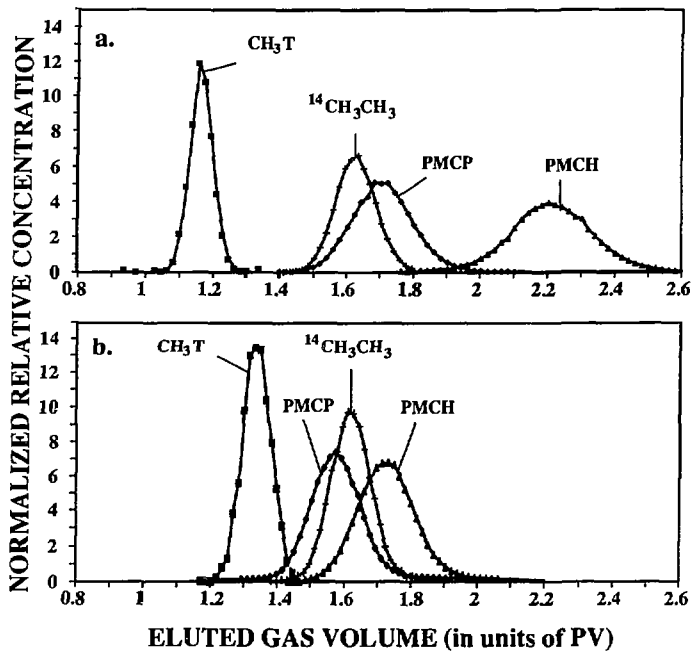


Fig.12



Institutt for energiteknikk (IFE) (tidligere Institutt for atomenergi) ble grunnlagt i 1948 og etablert som en uavhengig stiftelse i 1953. Hovedsenteret ligger på Kjeller. Virksomheten i Halden er konsentrert om det internasjonale OECD Halden Reactor Project. IFE er, med sine 540 ansatte, et av de største teknologiske forskningsinstitutter i Norge.

Institutt for energiteknikk (IFE) (formerly Institutt for atomenergi) was founded in 1948, and established as an independent foundation in 1953. The main center is located at Kjeller. The activities in Halden are concentrated on the international Halden OECD Reactor Project. IFE, with its 540 employees, is one of the major technological research institutes in Norway.

## AKTIVITETSOMRÅDER

- PETROLEUMSTEKNOLOGI
- KJERNEKRAFT
- PROSESSKONTROLL
- INDUSTRIELL ENERGITEKNOLOGI
- ENERGØKONOMISERING
- ISOTOPFORSYNING OG BESTRÅLING
- MATERIALTEKNOLOGI
- GRUNNFORSKNING I FYSIKK
- MILJØ- OG STRÅLEVERN

## SPESIALITETER

- NUKLEER BRENSSELSTEKNOLOGI
- SYSTEMSIMULERING
- MANN-MASKIN KOMMUNIKASJON
- INDUSTRIELL MATEMATIKK
- EFFEKTIV ENERGIBRUK
- RESERVOARMODELLERING
- PETROLEUMSGEOLOGI
- BASSENGMODELLERING
- TRACERTEKNOLOGI
- FLERFASE STRØMNING
- GASS MALETEKNIKK
- STRÅLINGSTEKNISKE INSTRUMENTER
- ISOTOPANALYSER
- RADIOFARMAKA
- BESTRÅLINGSTEKNIKK
- KORROSJON - EROSIJON
- AVANSERTE SVEISEMETODER
- FASTSTOFF FYSIKK
- RADIOLOGISK MILJØVERN
- RADIOAKTIVT AVFALL

## MAIN ACTIVITIES

- PETROLEUM TECHNOLOGY
- NUCLEAR POWER
- PROCESS CONTROL
- INDUSTRIAL ENERGY TECHNOLOGY
- ENERGY CONSERVATION
- ISOTOPE PRODUCTION AND IRRADIATION SERVICES
- MATERIALS TECHNOLOGY
- BASIC RESEARCH IN PHYSICS
- ENVIRONMENTAL AND RADIATION PROTECTION

## SPECIAL ACTIVITIES

- NUCLEAR FUEL TECHNOLOGY
- SYSTEM SIMULATION
- MAN-MACHINE COMMUNICATION
- INDUSTRIAL MATHEMATICS
- EFFICIENT ENERGY USAGE
- RESERVOIR MODELLING
- PETROLEUM GEOLOGY
- BASIN MODELLING
- TRACER TECHNOLOGY
- MULTI-PHASE FLOW
- GAS MEASURING TECHNIQUE
- RADIATION INSTRUMENTS
- ISOTOPE ANALYSES
- RADIOPHARMACEUTICALS
- IRRADIATION TECHNIQUES
- CORROSION - EROSION
- ADVANCED WELDING TECHNIQUES
- SOLID STATE PHYSICS
- RADIOLOGICAL PROTECTION
- RADIOACTIVE WASTE



PO Box 40 - N 2007 Kjeller, Norway  
 Telefon (06) 80 60 00  
 Teletax Admin (06) 81 61 56  
 Tech dep (06) 81 55 53  
 Tech dep (06) 81 11 68  
 Isotope dep (06) 80 02 10  
 Library (06) 81 09 20

PO Box 173, N 1751 Halden, Norway  
 Telefon (09) 18 31 00  
 Teletax Admin (09) 18 11 20  
 Tech dep (09) 18 31 03  
 Tech dep (09) 18 71 09