Location of Radiotracer Sampling

Pipeline inspection gauge

A Table Top Static Gas Sensing Unit
CONTENTS

Development and Application of Radiotracer Dilution Technique for Flow Rate Measurements
H.J. Pant, Jayashree Biswal, Sunil Goswami, J.S. Samantray, V.K. Sharma, K.S.S. Sarma and Shyam Shukla

Development of External Pipeline Inspection Gauge for Monitoring the Health of Industrial Carbon Steel Pipelines

Synthesis, Characterisation and Evaluation of Strontium Selective Crown Ether 4,4′(5′)-[di t-butylcyclclohexano]-18-crown-6
Snehasis Dutta, Sulekha Mukhopadhay, K.T. Shenoy and S. Mohan

A Table Top Static Gas Sensing Unit: Model No. TPD-BARC-16CH

Mahatma Gandhi Bharti ko Vijnani Upanishad Karna
Dr. Arvind K. Shrivastava

National Technology Day 2017

1
10
14
19
26
29
Development and Application of Radiotracer Dilution Technique for Flow Rate Measurements

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Radiotracer dilution technique for flow rate measurements in pipelines, canals, mountainous rivers, and streams was developed and applied for measurement of water flow rates in a branch canal of M/s Sardar Sarovar Narmada Nigam Limited (SSNNL), Surendranagar, Gujarat and in large diameter pipelines in a power plant at Vishakhapatnam, owned by M/s Hinduja National Power Corporation Limited (HNPCL), Vishakhapatnam, Andhra Pradesh. In case of the M/s SSNNL, Gujarat, the measurements were carried out to quantify the flow rates and validate the efficacy of the Concrete Volute (CV) Pumps used for pumping the water along the canal. Whereas in case of the M/s HNPCL, Andhra Pradesh, the flow rate measurements were carried out to check the calibration of the installed flow meters as well as to validate the efficacy of the Vertical Turbine (VT) pumps used for pumping water through the pipelines. Iodine-131 as potassium iodide was used as radiotracer in both the cases. The flow rates of water were ranging from 20.30±0.29 - 20.62±0.26 m³/s measured at four different pumping stations along the canal when single CV pump was operated. The measured flow rates were found to be in agreement with the theoretically estimated pumping capacity of a CV pump, i.e. 20 m³/s. The values of the flow rates measured in large diameter pipelines at M/s HNPCL, Visakhapatnam, ranged from 14.10±0.43 - 15.43±0.46 m³/s with single VT pump in operation and ranged from 24.55±0.78 - 27.51±0.82 m³/s when two identical VT pumps were operated simultaneously. The measured values of the flow rates were used to validate the efficacy of the pumps, calibrate the flow meters and optimize the pumping operations leading to significant revenue savings to the industries.

Introduction

The accurate knowledge of flow rates of process material (liquid, gas and solid) in industrial and environmental systems is an essential requirement. The flow rates are usually needed for one or more of the following reasons i.e. calibration of installed flow meters, in situations where flow meters are not installed, material balance, measurement of efficacy of pumps or turbines, distribution of flow in a network of pipes, etc. Generally, the industrial systems where the flow rates are needed to be measured are classified into two categories, namely open channels and closed conduits. Open channels are systems where the stream has a free surface open to the atmosphere such as canals, rivers, streams, sewer lines, effluent channels etc. Flow in closed conduits, such as pipelines is caused by a pressure difference. Various conventional methods such as gravimetric method, hydraulic structure method, velocity-area method or current meter method and slope-hydraulic radius method are used for flow rate measurements in canals, rivers and tunnels [1-8]. None of the above methods can be applied for flow rate measurement in all the situations. The selection of a suitable method for a particular application depends on the type and nature of the system, physical properties of the flowing water, flow patterns of the water, limitations imposed by the design and operating condition of the plant, cost and installation of the equipment. Similarly, various types of flow meters, such as ultrasonic, electromagnetic, acoustic, venturi, pitot tube, etc., are used for flow rate measurements in pipelines [9] in industry. Most of these flow meters have limitations in large diameter pipelines. Tracer dilution method is one of the most widely used and well-suited for flow rate measurements in canals and large diameter pipelines. The tracer dilution technique can be applied for flow measurements in irregular shaped, large diameter and fully or partially filled pipelines [1-18]. The dilution technique can also be used for flow rate measurement even when the flow path is branched. The tracer used could be either a chemical or a radioactive isotope. Chemical tracers such as fluorescent dye, normal salts are commonly used for measurement of flow rates in canals and pipelines. The measurement of high flow rates using chemical tracer requires large amount of tracers to be injected as they cannot be detected below a few milligram per litre. Injecting a large amount of tracer will affect the flow as well as contaminate the system. The fluorescent dyes such as Rodamine B, though detectable under high dilutions, are generally lost from the water medium through adsorption on the bed, walls and soil in suspension [13]. Some of these drawbacks of chemical tracers could be overcome by using radiotracers. The radiotracers are particularly useful for higher discharge rate (upto 1200 m³/s) measurements with better accuracy owing to their higher detection sensitivity (10⁻⁷ mg/cc) [11, 12, 14-16]. Because of this property of radiotracers, a few micrograms of radiotracer is sufficient. There is essentially no interference with the system being studied. The present article describes an application of radiotracer dilution technique flow measurements in a canal and large diameter pipelines to evaluate and validate the pumping efficacy of the pumps used for pumping the water and calibrate the installed flow meters.
Principle of tracer dilution technique

The principle of tracer dilution method is illustrated in Fig 1. A known concentration of radiotracer \( C_0 \) is injected into a stream (pipeline or canal) at a constant rate \( q \) over a sufficiently long duration of time. A downstream location is selected for collection of samples at which the tracer is homogeneously mixed known as the mixing distance with the entire cross-section, i.e., the variation of radiotracer concentration across the flow cross-section is less than 0.5 \%

The concentration of injected tracer is measured at a point beyond the mixing distance and a concentration-time plot is plotted (Fig.1). The region in the curve, where the tracer concentration becomes constant is known as the plateau region. Samples are collected for the measurement of radiotracer concentration after dilution \( C_2 \) from a downstream location beyond the mixing distance. The stream flow rate \( Q \) is computed from Eq. 1 for the conservation of mass as explained below. The background tracer concentration before tracer injection is \( C_1 \).

\[
qC_1 + QC_0 = (q + Q) C_1
\]

Since \( Q \gg q \), \( q + Q \approx Q \)

Also, \( C_2 \gg C_1 \)

Therefore, \( Q = q \times \frac{C_1}{C_2} \) \hspace{1cm} (1)

The sampling point at downstream location is critically dependant on the complete mixing of tracer across the cross-section of the flow. The mixing length \( L_m \) depends on the geometric dimension of the channel cross-section, discharge and turbulence levels. The mixing distance for open channel and closed conduit flow can be estimated experimentally as well as theoretically. Several empirical formulae have been reported in the literature for estimation of the mixing distance required for flow rate measurements in open channels \([1, 19-22]\) using tracers and formula gives the most satisfactory estimation of the mixing length (Eq. 2). Similarly, the mixing distance required for closed conduits is determined as per the guidelines specified in the standard ISO 2975, which is about 140 times the pipeline diameter \([23, 24]\). Rimmar's empirical formula \([1, 25]\) for mixing length \( L_m \) is given by,

\[
L_m = \frac{0.13\sqrt{b}C_2}{Qd}\frac{C}{\sqrt{2}}
\]

where, \( b \): mean width of the channel, \( d \): mean depth of the channel, \( C \): Chezy coefficient of roughness \((15 < C < 50 \text{ m}^1/2 \text{ s})\), \( g \): acceleration due to gravity. The above empirical formula (Eq. 2) was used for estimation of mixing length in the case studies described in this article.

There are ways to reduce the mixing length. This is possible by distributed injection, i.e, tracer is injected in several discrete points along the width of the channel. In case of flow measurements in pipelines, if the radiotracer is injected at the suction end of the pump, the mixing will be enhanced, thereby decreasing the mixing length.

The radiotracer should be injected continuously at a particular rate over a sufficient time period to establish an equilibrium concentration at the sampling point and to allow adequate time for collection of a few samples. The injection duration comprises of duration of sample collection and duration of buildup of the plateau \( t \) (Fig. 1). The duration of sample collection is estimated by the total number samples to be collected. In case of a straight measuring length and turbulent flow, \( t \) can be calculated from Eq (3) \([23]\).

\[
t = \frac{0.13\sqrt{b}C_2}{Qd}\frac{C}{\sqrt{2}}
\]

where, \( u \): mean velocity of the flow (m/s), \( x \): distance of sampling location from the injection point (m), \( D \): conduit diameter (m).
Radiotracer methodology

An ideal tracer is a substance that is intentionally introduced into a system, be it biological, industrial or environmental, to study the dynamics of the process material flowing through the system. The tracer quantity should be small and its introduction into the system should not disturb the flow. Further, it should be distinguishable from the process material for its detection. In case of a radiotracer, radioactivity is the property that distinguishes it from the bulk process material and enables its detection. Also, the tracer should not get adsorbed on walls of the system. In case of tracing a phase without any chemical reaction; the radiotracer should have physical properties similar to that of the process material being traced. But if a phase being traced involves a chemical reaction, the radiotracer should have physical and chemical properties identical to that of the phase being traced.

The procedure for flow rate measurement using radiotracer dilution method involves selection of a suitable radiotracer, estimation of amount of activity required for the measurements, preparation and its transport to the experimental site, continuous injection of a known amount of radiotracer at a constant rate, online monitoring of its concentration, sample collection at a downstream location, measurement of concentration in the injected and collected samples; and estimation of the flow rate. Some of the major steps involved are discussed below.

Selection of radiotracer

The selection of a radiotracer for a particular study requires careful consideration of various characteristics of the radiotracer such as physico-chemical behaviour, half-life, type and energy of radiation, possibility of production, specific activity and radiotoxicity. In majority of the industrial applications, the phase tracing does not involve a chemical reaction and thus only the physical properties of the radiotracer need to be considered. This enables the selected radiotracer to mix homogeneously within the phase being traced. For ‘in situ’ detection, a gamma-emitting radiotracer is selected and the energy of the emitted gamma radiation should be sufficiently high to penetrate through the wall of the system and get detected. Lower energy gamma emitting tracers are, on the other hand, easier to transport in view of their modest shielding requirement. The half-life of the selected radiotracer should be sufficiently long to prepare the radiotracer, transport it to the experimental site and complete the measurements; and at the same time it should be short enough to minimize any environmental hazards. The selected radioisotope used for preparation of the radiotracer should have sufficiently high neutron absorption cross-section to enable its production in desired quantities. Also, the selected radiotracer should have low radiotoxicity. The specific activity of a radiotracer is an important factor to be considered from the radiological safety point of view. One would usually

<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>Half-life</th>
<th>Major gamma energy, MeV (% abundance)</th>
<th>Chemical form</th>
<th>Tracing medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine-131</td>
<td>8.04 d</td>
<td>0.36 (80%) 0.64 (9%)</td>
<td>Sodium iodide</td>
<td>Water</td>
</tr>
<tr>
<td>Sodium-24</td>
<td>15h</td>
<td>1.37 (100%) 2.75 (100%)</td>
<td>Sodium carbonate</td>
<td>Water</td>
</tr>
<tr>
<td>Bromine-82</td>
<td>36 h</td>
<td>0.55 (70%) 1.31 (27%)</td>
<td>Potassium bromide,</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ammonium bromide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>p-dibromo benzene</td>
<td>Organic liquid</td>
</tr>
<tr>
<td>Technetium-99m</td>
<td>6 h</td>
<td>0.14 (90%)</td>
<td>Sodium pertechnetate</td>
<td>Water</td>
</tr>
<tr>
<td>Molybdenum-99</td>
<td>67 h</td>
<td>0.18 (4.5%) 0.74 (10%) 0.78 (4%)</td>
<td>Sodium molybdate</td>
<td>Water</td>
</tr>
<tr>
<td>Gold-198</td>
<td>2.7 d</td>
<td>0.41 (99%)</td>
<td>Chloroauric acid</td>
<td>Solid (Adsorbed)</td>
</tr>
<tr>
<td>Lanthanum-140</td>
<td>40 h</td>
<td>1.16 (95%) 0.92 (10%) 0.82 (27%) 2.54 (4%)</td>
<td>Lanthanum Chloride</td>
<td>Solid (Adsorbed)</td>
</tr>
<tr>
<td>Scandium-46</td>
<td>84 d</td>
<td>0.89 (100%) 1.84 (100%)</td>
<td>Scandium oxide</td>
<td>Solid (Particle)</td>
</tr>
<tr>
<td>Krypton-79</td>
<td>35 h</td>
<td>0.51 (15%)</td>
<td>Krypton</td>
<td>Gas</td>
</tr>
</tbody>
</table>

Table 1: Commonly used radiotracers used for flow measurements in industry and environment
transport small volume of the radiotracer to the experimental site as they are easy to shield and manoeuvre. But the injection of high specific activity poses a risk of loss of the tracer on the wall of the system. The probability of such risk is greatly reduced by adding a carrier i.e. non-radioactive counterpart to the injected tracer. The commonly used radiotracers used for flow rate measurements of different phases in industrial and environmental systems are given in Table 1. Based on the above considerations, Iodine-131 as NaI was selected and used as radiotracer in the case studies described in this article.

**Amount of radiotracer**

The amount of radiotracer required to measure flow rate is estimated by considering the detector sensitivity for a specific radioisotope at a chosen detection geometry, accuracy desired, expected dilution between the injection and the measuring location and natural background radiation. The detector sensitivity (counts per unit time per unit volume per unit radioactivity) is estimated in the laboratory prior to the field measurements. To minimize possible loss of radiotracer due to adsorption on different surfaces, a non radioactive carrier (similar chemical properties as the radioactive tracer) is always added to the tracer solution before injection.

Based on the above considerations, about 55 GBq activity of Iodine-131 was estimated to be used for flow rate measurements in the canal. Similarly, the amount of radiotracer required for the flow rate measurements in the pipelines was estimated to be about 11 GBq when only one pump was operated and 22 GBq when two pumps were operated.

**Preparation of radiotracer**

The radiotracer is prepared by neutron irradiation of a suitable target material in a nuclear reactor followed by chemical processing (if required). The target material is chosen in such a way that, it should undergo nuclear reaction with thermal neutrons to produce the desired radiotracer with appreciable yield. The yield of the product radioisotope depends upon amount of starting material, natural abundance of the target isotope and cross-section of the nuclear reaction. Iodine-131 (\(^{131}\text{I}\)) in the form of sodium iodide has been used as radiotracer in the two case studies reported here. Hence the preparation of \(^{131}\text{I}\) radiotracer is explained below. An accurately weighed tellurium dioxide (\(\text{TeO}_2\)) powder was irradiated in DHRUVA reactor at a thermal neutron flux of \(5 \times 10^{17} \text{n cm}^{-2} \text{s}^{-1}\) for 21 days. After the irradiation, the can was cooled for 2 days and was transported to the radiochemical processing laboratory in a lead shielded flask. \(^{131}\text{I}\) is produced by \(^{130}\text{Te}(n,\gamma)^{131}\text{Te}\) nuclear reaction (\(\sigma_n = 200 \text{ mb}\)) followed by beta decay. The \(^{131}\text{I}\) radioisotope was separated from the target by dry distillation. \(^{131}\text{I}\) is dissolved in aqueous solution and exist in the form of sodium iodide.

**Case studies**

The radiotracer dilution method was used for flow rate measurements of water in a branch canal of a canal system and large diameter pipelines in a power plant. The two case studies are described below in details.

**Flow rate measurements in a canal**

The Sardar Sarovar Project (SSP) shown in Fig. 2, Gujarat, India, an inter-state and multipurpose river valley project irrigates Gujarat, Rajasthan and Maharashtra, provides drinking water to a large number of villages in Gujarat and generate hydropower. The project consists of a main terminal dam on the river Narmada along with 30 major dams, 135 medium dams and 3000 minor dams, a canal system and two

![Fig. 2: Site map and location of the canal](image_url)
hydropower stations. The canal system consists of 532 km Narmada Main Canal, with a capacity of 1133 m$^3$/s at the head regulator 38 branch canals taking off from the main canal, covering a total length of 75,000 km, supply to about 2 million hectares of land. The Saurashtra Branch Canal (SBC) is the largest branch canal of Narmada Canal system, which takes off from the Narmada Canal near the village Karannagar. The SBC is 104 km long and tails into Bhogavo II reservoir (Dholi Dhaja Dam) near Surendranagar (Fig. 2).

For supplying water to Saurashtra and Kachchh regions where natural terrain prevents gravity flow, huge pumping stations have been provided at different locations. On the SBC, the total lift of 71 m is provided by a series of five pumping stations with pumping head ranging from 10.8 m to 17 m. In these pumping stations, a total of 26 Concrete Volute (CV) Pumps each having capacity of 20 m$^3$/s and 22 Vertical Turbine (VT) Pumps each of 5 m$^3$/s capacity are installed. After design, engineering, construction and commissioning of all five pumping stations one of the mandatory requirements was to measure discharge rate for validation of efficiency of the installed CV pumps, energy auditing, and effective management and distribution of water.

The radiotracer dilution method was used for measurement of flow rates in four different sections of SBC. Five pumping stations (PS1, PS2, PS3, PS4 and PS5) were constructed along the 104 km long section of the SBC canal and used for pumping water. Fig. 3 shows a typical pumping station used for pumping the water through the canal and the crosssection of the canal. Each pumping station comprises of 5-6 identical CV pumps. The flow rates were measured at four pumping stations PS2, PS3, PS4, and PS5 with single pump in operation at each station.

For each test, the radiotracer solution was prepared by diluting the radiotracer containing 55 GBq activity of $^{131}$I in a volume of 15 litre of water in a graduated cylindrical vessel. About 0.06% inactive potassium iodide and 0.3% of sodium thiosulphate was also added and homogeneously mixed within the solution to minimize the losses due to adsorption and evaporation, respectively. 20 ml of this solution was withdrawn, further diluted to a volume 20 L in three successive steps with a dilution factor of 10$^7$ and stored for the measurement of $C_0$. The prepared radiotracer solution was injected at the suction end of the pump at a known constant rate ($q$) (Table 2) as shown in Fig 4. The injection rate was also manually estimated by monitoring the reduction in volume of tracer solution with time as shown in Fig 5.

The samples for measurement of radiotracer concentration ($C_t$) were collected from a downstream location (Fig 3b) at which the radiotracer was expected to mix homogeneously.
within the entire cross-section of the canal. For the present case, the mixing length required for the radiotracer to mix homogeneously with the entire cross-section was estimated to be about 405 m.

However, the samples were collected from downstream locations i.e. about 900-2700 m away from injection point. Therefore, sufficient mixing length was provided for radiotracer to mix homogeneously across the cross-section of the canal. The radiotracer concentration in the injected solution ($C_i$), collected samples ($C_c$) was measured using a specially fabricated sampling vessel (20 L) mounted with a NaI(Tl) scintillation detector connected to a data acquisition system. The sampling vessel and the data acquisition are shown in Fig 6 and Fig 7, respectively. The detector was set to record tracer concentration at an interval of 2 minutes during the sample measurement. Identical detection geometry and conditions were maintained during measurement of tracer concentration in injected solution ($C_i$) and samples collected from monitoring locations ($C_c$). Similar experimental procedure was adopted in all four flow measurement tests. The flow rates measured at four pumping stations of the canal with a single CV pump in operation at each station are given in Table 2 and were found to be ranging 20.30±0.29 - 20.62±0.26 m$^3$/s. The measured values of flow rates at four different pumping stations were found to be in good agreement with the theoretically estimated discharge rates of the respective pumps.

**Flow rate measurements in large diameter pipelines**

The flow measurements were carried out in two large diameter pipelines in a coal based thermal power plant at M/s Hinduja National Power Corporation Limited (HNPCL), Vishakhapatnam, Andhra Pradesh, India. The plant has two units (Unit-1 and Unit-2) each of 520 MW capacity. Steam produced in the plant is fed into the steam turbine at high pressure and temperature for generation of electric power. The exhausted steam is condensed in condensers and fed back into the boiler for reuse. Sea water is pumped through two different pipelines, each of diameter 3.6 m, using Vertical Turbine (VT) pumps and circulated through the condensers for steam condensation. A typical pipeline is shown in Fig.8.

![Fig. 6. Setup for off-line measurement of radiotracer concentration](image6)

![Fig. 7. Multi-input data acquisition system (MIDAS) with a NaI(Tl) scintillation detector](image7)

<table>
<thead>
<tr>
<th>Pumping station, PS2</th>
<th>$C_i$ (counts/2 min)</th>
<th>$C_c$ (counts/2 min)</th>
<th>Q (m$^3$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>135.00</td>
<td>5.662 x 10$^7$</td>
<td>6275</td>
<td>20.30±0.29</td>
</tr>
<tr>
<td>156.00</td>
<td>9.304 x 10$^7$</td>
<td>11760</td>
<td>20.62±0.26</td>
</tr>
<tr>
<td>143.81</td>
<td>2.197 x 10$^7$</td>
<td>25811</td>
<td>20.47±0.22</td>
</tr>
<tr>
<td>144.07</td>
<td>1.0426 x 10$^7$</td>
<td>12179</td>
<td>20.60±0.37</td>
</tr>
</tbody>
</table>

Table 2: Results of flow rate measurements in the canal
A schematic diagram of the experimental system is shown in Fig 9. There are two independent pumping stations for each unit and each pumping station has two identical VT pumps for pumping the sea water for cooling. The pumps, P1A and P1B are used for pumping water in Unit-1, whereas the pumps P2A and P2B are used for pumping the water in Unit-2. Four tests were performed with operations of P1A; P1A and P1B simultaneously; P2A; and P2A and P2B simultaneously for flow rate measurements. The radiotracer stock solution preparation and the tracer injection were carried out in a similar manner as mentioned in previous case study described in the current article. In this case about 11-22 GBq activity of \(^{131}I\) was used in each measurement. The radiotracer injection system used for injecting the radiotracer into the pipeline is shown in Fig 10.

An aliquot of 20 ml was collected from the stock solution, further diluted to a volume 20 L in three successive steps with a dilution factor of \(10^3\) and stored for measurement of \(C_1\). The samples for the measurements of tracer concentration \(C_r\) were collected from a downstream location at a distance of 1500 m from the injection point. This distance was sufficient enough for the radiotracer to mix uniformly across the cross-section of the pipe. The concentrations of radiotracer in injected solution and in sample collected at downstream were measured as mentioned in Section 4.1. The results obtained from the flow rate measurements in large diameter pipelines in the thermal power plant are given in Table 3.

### Table 3: Results of flow rate measurements in large diameter pipelines

<table>
<thead>
<tr>
<th>Unit</th>
<th>q (ml/min)</th>
<th>(C_1) (counts/2 min)</th>
<th>(C_r) (counts/2 min)</th>
<th>(Q) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit-1, P1A</td>
<td>188.2</td>
<td>5.867 (x) (10^7)</td>
<td>11875</td>
<td>15.43±0.46</td>
</tr>
<tr>
<td>Unit-1, P1A+P1B</td>
<td>187.2</td>
<td>3.755 (x) (10^5)</td>
<td>4240</td>
<td>27.51±0.82</td>
</tr>
<tr>
<td>Unit-2, P2A</td>
<td>220.8</td>
<td>3.096 (x) (10^5)</td>
<td>8044</td>
<td>14.10±0.43</td>
</tr>
<tr>
<td>Unit-2, P2A+P2B</td>
<td>185.1</td>
<td>6.626 (x) (10^7)</td>
<td>8291</td>
<td>24.55±0.78</td>
</tr>
</tbody>
</table>

The values of the flow rates of cooling water in the pipelines of Unit-1 and Unit-2 of the power plant were measured to be 15.43±0.46 and 14.10±0.43 m/s, respectively when only one VT pump was operated in each unit. Whereas, the values of the measured flow rates were found to be 27.51±0.82 and 24.55±0.78 m/s, respectively when both the pumps were operated simultaneously in each unit. To the best of author's knowledge the flow rate measurement in such large diameter pipelines using radiotracer dilution technique has been carried out for the first time.

### Radiological safety

The radiotracer tests were carried out by trained and authorized personnel of Isotope and Radiation Application Division (IRAD), Bhabha Atomic Research Centre, Mumbai.
with prior approval Atomic Energy Regulatory Board (AERB). The radioactive waste generated was stored in a suitable container and placed in an isolated room to allow the activity to decay before disposal. The general guidelines for safe handling and use of radioisotopes issued by International Commission on Radiological Protection (ICRP) and AERB were followed during the investigations. In current investigation, the injected radiotracer was diluted in large volume of water and the concentration of Iodine-131 in the water was much below than the prescribed limit. Therefore, the injected radiotracer did not pose any radiation hazardous to the public and environment.

Conclusions
The radiotracer dilution technique was developed, standardized and successfully applied for measurements of water flow rate in two large-scale industrial systems i.e. canal and large-diameter pipelines. The values of the flow rates measured in the two systems were found to be in good agreement with the theoretically estimated values of the respective pumps. This lead to the conclusion that both types of pumps behaved as per the design criteria. The flow rate measured in the SBC canal at M/s SSNNL, Surendranagar, Gujarat, were used to optimize the pumping operation, water distribution through various branch canals and energy consumption and; water budgeting.

In case of flow rate measurements in large diameter pipelines at M/s HPNCL, Vishakhapatnam, Andhra Pradesh, the values of the flow rates measured by the installed flow meters were found to be significantly different from that of the values measured using radiotracer dilution technique. This implied that either the calibrations of the installed flow meters were altered during the operation or the flow meters were malfunctioning. Subsequent to the flow rate measurements using radiotracer dilution technique, the installed flow meters were uninstalled and found to be malfunctioning. The flow meters were repaired, recalibrated and installed back on the pipelines. After the reinstallation of the flow meters, the values measured by the flow meters were found to be in good agreement with the values measured using the radiotracer dilution technique.

The application of the radiotracer dilution technique helped, to validate the efficacy of the two different types of the pumps, to calibrate the installed flow meters, optimize the pumping operation and water distribution leading to significant economic benefits to both the industries. The technique proved to be sensitive and versatile for flow measurements; and can be applied for accurate measurement of flow rates in systems were conventional methods cannot be used.

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The authors wish to thank the authorities of M/s Kirloskar Brothers Limited, Pune; M/s Sardar Sarovar Namada Nigam Limited (SSNNL), Surendranagar, Gujarat and M/s Hinduja National Power Corporation, Visakhapatnam, Andhra Pradesh for providing necessary logistic support and help in conducting the flow rate measurements.

References


BARC has developed a fleet of Instrumented Pipeline Inspection Gauges (IPIGs) for health monitoring of buried carbon-steel pipelines carrying petroleum product. These tools, once inserted into the pipeline, travel with the cargo without disturbing the throughput and record MFL signals emanating from the pipe surface. However, there are pipelines in oil refineries, process industries and power plants (conventional and nuclear) where inspection from inside is not possible/ (which are unpiggable from inside). These lines are mostly inspected at few locations during in-service inspection schedule, but full periphery and full length inspection coverage is not feasible due to the unavailability of any standard inspection tool. Nevertheless, integrity management of such pipes are of paramount importance. A novel inspection tool known as External PIG (EPIG) has been developed for 6” NB liquid waste discharge pipeline of IF3. The tool inspected the line and produced encouraging results. The results have been verified independently at several locations. The tool is light weight, easy to handle and can do quick inspection of the pipeline from outside. This paper outlines the development work of EPIG from inception to field trials with inspection results.

Introduction

Over the years, BARC has developed a fleet of in-line-inspection (ILI) tools ranging from 12” to 24” for in-line inspection of buried oil pipelines. These tools are now commercially available in the country and are being extensively used for health monitoring of cross country pipelines of IOCL and other PSUs. Using the expertise and domain knowledge in the area of in-line inspection, a magnetic flux leakage (MFL) based External pipeline inspection gauge (EPIG) has been developed for inspection of 6” pipeline of IF3, BARC. The tool inspects the pipeline externally for both near wall (external surface) and far wall (internal surface) defects. These pipelines are usually inspected at specific locations, but are never inspected for full length with 100% peripheral coverage due the lack of standard inspection tool or available methodology. Recently, research has been directed towards this area with an attempt to build automated robots with magnetic wheels to scan pipe surface externally [1]. The tool scans a small sector of a large diameter pipeline, while moving autonomously over the pipe surface. Similar non-autonomous tools with spot classification capability (go/no-go) and much lower sensitivity are also available commercially [2]. However, none of the developments point towards a comprehensive full-periphery pipeline inspection technique and defect characterization methodology.

In the present development, a tool, split in two halves, is designed to scan the full periphery of the pipe externally. In the presence of a corrosion (metal loss) defect, the leakage flux near the defect will increase and in turn is sensed by a series of hall-effect sensors spanning the full-periphery. The signal is observed in near real-time as well as stored for offline analysis.

EPIG development

Basic Principle

MFL signals are widely used for non-destructive evaluation (NDE) of defects in carbon steel petroleum cross-country buried pipelines. The principle involves magnetizing a section of pipe to near saturation and sensing the leakage flux at the magnetic neutral plane with hall-effect sensors. In presence of corrosion defect or gouging or any other pipeline feature, e.g. welds, flanges etc the leakage flux signature would change, indicating the presence of anomaly [3].
Tool development
The EPIG tool contains magnetizer, sensors, support rollers and odometers. Acquisition cum processing electronics and power supplies are housed in a separate casing outside the tool. The design of the tool has evolved iteratively through Finite Element (FE) modelling to optimize the magnetic saturation level inside the pipe. Challenge of the design was to ensure ease of tool handling while maintaining uniform magnetization level around full-periphery of pipe. Fig. 1 shows magnetization baseline inside the pipe for two such design trials, (a) a three module magnetizer and (b) a four module magnetizer. It shows that four module design yields more uniform magnetic field of higher strength and hence, it is adopted for final tool design. The complete FEM simulation of the 4 module tool is shown in Fig. 2 The pipe section between pole faces as shown in the Fig. 2 indicates the uniformly magnetised inspection area. A defect of known dimension (a full periphery slot of known depth and length) is made at the centre of this inspection region, and expected leakage flux profile is estimated at various lift-offs from the pipe surface. This gives an estimate of the leakage flux expected to be measured by sensors at various lift-offs. Effective design needs to ensure that any component in the magnetic circuit should not go into deep saturation. The flux level at various locations on the pipe surface as well as on the magnetiser is also noted. This helps in finalizing the mechanical dimensions of the magnetizer unit.

The EPIG tool is pulled over the pipe surface at a desired speed by a battery operated winching mechanism. Data is acquired with a desired sampling rate using hybrid sensing system with radial and axial MFL sensor arrays. Signals from these sensors are acquired and recorded by an in-house developed multi-channel data acquisition system (DAS). The system connects to a laptop for a near real-time viewing of the processed sensor data as well as its storage for offline analysis. Odometer system provides accurate localization of any pipe feature or corrosion defect that may get detected.

Defect characterisation
Defect templates with known sizes of faults were created on a 1 meter pipe spool and signals were recorded and analysed for generating data-bank. Fig. 3 shows the radial MFL signal recorded from a template defect by an array of sensors passing over it. The data-bank thus generated from these tests, were used to extract MFL signal parameters. As shown in the zoomed images in Fig. 3 the signal parameters extracted are (a) span measured in number of samples, (b) numbers of sensors sensing the defect (estimated from circumferential flux profile) and (c) maximum peak to peak leakage flux recorded by the centremost sensor. These signal parameters are then mapped to defect parameters using an empirical model. More details on signal parameter extraction can be found in [4]. An empirical model is trained based on template data and used for mapping the signal parameters to defect parameters (length, width, %WL).
Inspection of liquid waste discharge pipeline at IF3, results and validation

The tool was deployed in field to inspect 6” liquid waste discharge pipeline of IF3, BARC. The complete tool with its sensor arrangement and winching mechanism is shown in Fig. 4 and Fig. 5 respectively.

A total of 59 spools of the pipeline were inspected on a spool by spool basis. The entire inspection took 2 days to complete, with an average of 7-8 minutes inspection time per spool. The total length of inspection is about 250 meter. The schematic map of the inspection area is shown in Fig. 6. The only limitation of the EPIG tool is that it cannot inspect the pipe section at support locations. The tool is dismantled at supports and is again re-assembled for inspection of the next section. However, downtime is only of the order of few minutes (typically 4 – 5 min). The signals from MFL sensors over each spool is observed in near-real time and recorded for further offline analysis. The data recorded from each spool is converted into an image of the pipe surface (C-scan). The C-scan is generated after de-noising the signal using discrete wavelet transform with thresholding [3]. Such a C-scan can be seen in Fig. 7. A weld and a metal loss (corrosion) defect (very close to the weld in the upper section) are clearly seen in this image. These are reported, along with its location from the start of the spool. For each metal loss defect, the feature parameters are extracted as explained in Section 2.3 for estimating the defect sizes (length, width and percentage wall-loss).

Based on the report, few severe defects are chosen for site verification. These defects are visually verified (if they are external) and sized with vernier depth gauge measurement or measured with an ultrasonic thickness gauge (for internal defects). From the field run of EPIG, estimated dimensions (length, width and percentage wall loss) of 5 defects were successfully verified on site (including one internal defect).

Three external defects along with their C-scans can be seen in Fig. 7 (one) and Fig. 8 (two). One internal defect can be seen in Fig. 9 (upper section, right of the weld). Defects were found at the precise location estimated by odometer data. The estimated defect parameters and its site-verified measurements are given in Table 1 along with their percentage error. The defects 1 through 4 are external and verified by vernier measurement and 5th defect is internal, and is verified by ultrasonic gauge.

The error observed is well within acceptable limits as per Pipeline Operators Forum (POF) requirements. The site verification of reported results builds good confidence in overall inspection capability of EPIG. The out of bound errors observed can be reduced further with multiple field trials and by employing more accurate site defect verification gauges.
Conclusion

The EPIG is a prospective tool for the inspection of carbon steel pipelines from outside. It gives almost full length and full periphery inspection coverage as compared to spot inspection with conventional technique. The ease of assembly and dismantling of the EPIG gives it the necessary advantage to inspect even physically inaccessible areas of pipeline. The tool can be used with minimum modifications to inspect carbon steel pipelines of different sizes existing in various plants and facilities in BARC and other DAE units.

Acknowledgement

The authors are grateful to Shri D. Das, AD (E), E&IG for his encouragement and support in pursuing specialised NDT applications being developed for BARC and other DAE units. The authors are thankful to Shri V K Gautam and his team from IF3 for their extensive support during inspection trial and site verification of the tool. Special thanks are also due to the South Gate Security personnel for facilitating access to the inspection area during several trial runs.

References

### A Table Top Static Gas Sensing Unit: Model No. TPD-BARC-16CH


Technical Physics Division

Table Top Static Gas Sensing Unit (Model: TPD-BARC-16CH) has been designed and developed. This unit is suitable for monitoring or recording the response of 16 sensing elements simultaneously under controlled conditions of operating temperature and gas environment. The indigenous software has also been developed that interfaces the instrument to a personal computer or Laptop. Moreover, the resistance of the sensing elements under investigations is recorded and displayed as a function of time. The unit can measure the resistance variation from 1 G to 1 K or 1 M to 1 . The developed product is unique and no such similar product is available in the market. Importantly, the instrument is useful for the measurement of response curves of chemiresistive sensors.

**Keywords:** Multiple Sensors Testing Unit, Gas Sensors, Operating Temperature, Data Acquisition

### Introduction

Gas sensing is one of the most widely investigated activities of the materials research [1]. With the advent of nanoscience and nanotechnology novel materials with superior performances are being routinely synthesized [2]. Development of gas sensors based on these materials demands a thorough investigation of these materials under controlled conditions of operating temperature and gas environment [3-4]. Further, to speed up the time for process optimization, simultaneous measurement of multiple sensors under identical conditions is desired but it often requires a very long time. In order to speed up the parameter optimization e.g. sensitizer, its concentration and annealing schedule, it is essential to have a system possessing the capability of recording the response curves under identical conditions of operating temperature and gas environment. To address this need, Technical Physics Division (TPD) has developed a Table Top Static Gas Sensing Unit (Model: TPD-BARC-16CH), which can monitor the responses of 16 sensing element simultaneously. The developed unit is suitable for monitoring or recording the response under controlled conditions of operating temperature and gas environment. Some of the salient features of this product are;

#### Technical Specifications of the unit

| Unit: TPD-BARC-16CH | 230 V, 50 Hz AC  
<table>
<thead>
<tr>
<th></th>
<th>Light weight (&lt;2 kg), portable</th>
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<tbody>
<tr>
<td><strong>Test Chamber 1:</strong></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>SS-304</td>
</tr>
<tr>
<td>Housing diameter</td>
<td>28 mm</td>
</tr>
<tr>
<td>Housing length</td>
<td>50 mm</td>
</tr>
<tr>
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<td>Array</td>
</tr>
<tr>
<td><strong>Test Chamber 2</strong></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>SS-304</td>
</tr>
<tr>
<td>Housing diameter</td>
<td>81 mm</td>
</tr>
<tr>
<td>Housing length</td>
<td>48 mm</td>
</tr>
<tr>
<td>Sensor types</td>
<td>Individual</td>
</tr>
<tr>
<td><strong>Technical Parameters:</strong></td>
<td></td>
</tr>
<tr>
<td>Resistance range</td>
<td>MΩ to Ω or GΩ to kΩ</td>
</tr>
<tr>
<td>Operating temperature range</td>
<td>RT to 300 ± 2°C</td>
</tr>
<tr>
<td>Control Software</td>
<td>Arduino IDE compatible with Labview</td>
</tr>
<tr>
<td>Acquisition type</td>
<td>Simultaneous</td>
</tr>
<tr>
<td>Data acquisition mode and speed</td>
<td>Adjustable, maximum 4 points/sec</td>
</tr>
</tbody>
</table>
• Uniquely positioned product: No such unit in the market is available containing both data acquisition and testing facility in one unit.

• Light weight and portable.

• Six order changes in the resistance can be measured (G - K).

• Two separate test chambers for multiple sensor array (10-16 numbers) and individual sensing element (maximum 7 numbers) testing, respectively.

• Operating temperatures can be tuned in the range from room temperature (RT) to 300°C.

• Real time monitoring with direct interface to personal computer or Laptop.

• Indigenous software, provision to select and deselect the sensing element.

The unit essentially comprises of the following two parts:
• Sensor test chambers and
• Data acquisition unit

Sensor test chambers
As shown in figure 1, the unit is equipped with two test chambers containing heaters and readers. The heater temperatures are controlled using potentiometer on the temperature control circuit in the housing below test chambers.

Test chamber 1
In this, two sensor arrays comprising of 5 sensing elements each with two heaters and two readers are provided. It consists of a Teflon disc containing an array (20 x 2) of gas tight electrical feed-through with a spacing of 1.5 cm (figure 2). For measurement of resistance of a sensor array of dimensions 1.5 cm x 3 cm, it is advised to connect heaters at the two edges along with readers. Heaters are made by connecting two Pt-100’s in parallel to each other, while reader is just a single Pt-100 whose resistance value as measured using digital multimeter is an indicator for the operating temperature.

The rest of the feed-throughs are connected to the data acquisition card located in the housing below.

Test Chamber 2
It consists of seven Teflon heads fixed in stainless steel (SS 304) disc as shown in figure 3 (a). The Teflon heads are provided with 6 pins (phosphor bronze) for electrical connections. Out of these 6 pins, two are used for sensing element, two for the connection of heater and the rest two for the reader as shown in figure 3 (b). The heater wires are connected to the temperature control circuit, reader wires to the 8-pin band change switch and the two sensing element wires to the data acquisition card. Here also, the heater is realized by connecting two Pt-100’s in parallel. The heater and the reader Pt-100’s are physically connected adjacent to each other so as to form a platform on which the sensing element can conveniently be rested. The heater and reader wires are connected to the phosphor bronze pins in such a way that a direct contact with the Teflon base is avoided.

Figure 4 shows the photograph of the wiring behind the test chambers. Herein color code has been followed, red color wires are used for heater, orange for reader and other colors for the sensing element. As is evident all the heater and reader are routed to the temperature control circuit and the 8-pin band change switch (digital...
multimeter) via a general purpose printed circuit board (PCB).

The stainless steel test chambers are provided with two values (inlet and/or outlet). The test volume of the chambers is 250 sccm (standard cubic centimeter). By injecting the known amount of test gas in the chamber through an inlet value provided with septum the concentration of the test gas can be controlled. For recovery measurements, the sensor chamber cap or top needs to be opened subjecting the sensors to the ambient environment. Importantly, the test chambers can be customized to specific needs of the user. Two pairs of either test chamber 1 or 2 can be used with necessary modifications of the wiring or connections.

**Operation of the Instrument**

Figure 5 shows the Home screen with various fields. There are three main tabs Data Acquisition (DAQ), settings and retrieval. There are 16 channels (0-15) displaying the resistance values (in k\(^\Omega\)) of the 16 sensing elements. The color of each channel is different and hence can be used to locate the channel on the screen. The individual sensing element can be selected or
deselected as per the requirement in the channel selector. In the settings, tabs options are provided to control or calibrate the data acquisition values (resistance) by setting the multiplication factor (x factor). By default it is set at 1.39. It is also possible to control the data acquisition speed by setting the Analogue to digital Converter (ADC) values. By default it is set at 30, it can be brought down to increase the data acquisition speed. The retrieval window is also provided to retrieve the previously saved data for comparison or reference, as and when required. The files can be recalled by pressing the retrieve data knob and locating the files through drop down menu.

Measurement of Response Curves

Once the sensors are mounted and the operating temperature is fixed, the chamber is closed and a settling time of 15 min is provided. Now, the known concentration of the test gas is injected using an air-tight syringe in the test chamber and the variation in the resistance as a function of time is recorded and monitored. Upon injection of the test gas, the resistance of the sensing element will increase or decrease depending upon the sensing element and the nature of test gas. For example, for n-type metal oxides like SnO₂, ZnO, and TiO₂ the resistance will decrease or increase when exposed to reducing (H₂S, NH₃) or oxidizing gases (NO₂, CO₂), respectively (Figure 5 (a) and (b)). Opposite is the case with p-type materials i.e. with holes as majority carriers. By default the files are saved as “.xls” file (excel) with the name as date and time of measurement. With columns showing the different channels and the rows depicting the resistance values. The first column is the time displayed in seconds. Moreover, the files can easily be accessed and transferred or copied to the other software as per the user requirement.

In order to demonstrate the working of the instrument a multiple sensor array (MSA, 12 sensing elements) based on ZnO nanowires has been tested for its response towards different gases and the results are shown in figure 6. For this ZnO nanowires were deposited using a

![Fig. 5: The real time response curves recorded using the unit for the n-type metal oxide sensors upon exposure to (a) oxidizing (NO₂) and (b) reducing gas (H₂S), respectively.](image)

![Fig. 6: (a) Variation of resistances of the MSA upon exposure to increasing concentration of NO₂ and (b) Zoomed response curve for the sensing element with smaller response values.](image)
hydrothermal method [3] and an array of (4 x 3) sensor films were realized by modifying the nanowire film with sensitizers namely Al, Ti, and Au layer. Figure 6 shows the response curves of all the 12 sensing elements towards increasing concentration of NO₂ between 1 and 25 ppm. The data was acquired using the instrument and plotted using the origin software.

As shown in figure 6, the 12 sensing elements were tested under identical conditions and accordingly it becomes easier to compare the response curves and the related parameters namely response time, recovery time, sensor response values in a single run. This implies that in a single exposure, it is possible to generate more information that can be used to tune the parameters to realize a better sensing material. Thus the result clearly demonstrates that the present system is capable of speeding up the parameter optimization in order to achieve the required sensing characteristics.

**Conclusion**

A uniquely versatile import substitute product namely a table top static gas sensing unit has been successfully developed, tested and implemented for addressing needs of a client base comprising of universities and other Research & Development institutes. The developed system can record response curves from the 16 sensing elements simultaneously. Two independent test chambers, one for the sensor array and the other for the individual sensing element have been provided. The operating temperature can be tuned right from RT to 300°C. The unit can measure the six order change in resistance from 1 GΩ to 1 KΩ or 1 MΩ to 1 Ω. Importantly, the product demonstrated its utility in speeding up the parameter optimization to achieve required sensing characteristics.

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**References**

Synthesis, Characterisation and Evaluation of Strontium Selective Crown Ether 4,4'(5')-[di t-butyldicyclohexano]-18-crown-6

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4,4'(5')-[di t-butyldicyclohexano]-18-crown-6 has been synthesised, as a highly selective ligand for Sr. The process involves the synthesis of 4,4'(5')-[di t-butyldibenzo]-18-crown-6 from which, 4,4'(5')-[di t-butyldicyclohexano]-18-crown-6 is synthesised by heterogeneous catalytic hydrogenation. This study portrays the role of the composition of the reaction medium on chemo-selectivity and yield of hydrogenation. The catalyst used in the hydrogenation i.e., 5% rhodium supported on γ-alumina, was synthesised in house and was characterised. Evaluation of the synthesised ligand was carried out through studies on extraction of Sr from simulated acidic high level waste. The synthesized ligand is found to be very effective for this role.

Introduction

Sr\textsuperscript{90} is produced as a fission product with its yield from U\textsuperscript{235}, U\textsuperscript{233}, and Pu\textsuperscript{239} being 5.7%, 6.6%, and 2.0% respectively [1]. It is a emitter (t\textsubscript{1/2} 28.8 yrs, 0.546 MeV) and decays to Y\textsubscript{90}, also a emitter (t\textsubscript{1/2} 64 hrs, 2.28MeV) which decays to stable Zr\textsuperscript{90}. Removal of Sr\textsuperscript{90} and Ca\textsuperscript{137} from High Level Waste (HLW) may eliminate the challenges of high decay heat in immobilisation of HLW. The commercial use of Sr\textsuperscript{90} is also significant. Y\textsubscript{90}, is used as a blood irradiator for treatment of bone cancer; Sr\textsuperscript{90} has application as energy source at remote locations and in Radiosotope Thermoelectric Generator (RTG) in spacecraft.

High selectivity and affinity for strontium has led to the use of 4,4'(5')-[di t-butyldicyclohexano]-18-crown-6 (DTBDB18C6) in recovery of Sr from radioactive waste solution [2]. With two tertiary butyl groups it has high oleophilicity. Also, its high radiation stability and low aqueous solubility makes it suitable to be used in commercial plant for Sr recovery. This ligand was first synthesised and used for the recovery of Sr\textsuperscript{90}, in 1990 [3, 4]. In this paper we elucidate the detailed synthesis of 4,4'(5')-[di t-butyldicyclohexano]-18-crown-6. The effect of the composition of the reaction medium on the chemo-selectivity and yield of the hydrogenation reaction has been studied. The hydrogenation catalyst i.e., rhodium supported on γ-alumina was prepared using a novel route. This work also depicts the strontium extraction performance of the synthesized ligand from HLW. The effects of various organic diluents used in solvent extraction of strontium with the ligand, have been demonstrated.

The reaction is carried out in a glass reactor, with the drop-wise addition of a combination of KOH (1-2M) and tert-butyl catechol (TBC, 1M) in butanol, to a solution of bischloroethyl ether (BCE) dissolved in butanol. The reaction takes place in a nitrogen environment, under reflux condition at 116 °C. The drop-wise addition of TBC is done in 2 steps, each addition step is carried out for 3-4 hrs and there is a time lag of 3 hrs between the steps. 24 hrs after the dropwise addition process, the reaction mixture is treated with KOH, and refluxed for additional 44 hrs. After which the excess KOH is neutralised by HCl addition, and butanol is recovered using a Rota-evaporator.

Fig. 1: Reaction for the synthesis of 4,4'(5')-[di t-butyldibenzo]-18-crown-6 (DTBDB18C6) – 'the precursor'
Purification of crude 4,4'(5')-[di t-butyldibenzo]-18-crown-6

The product formed through the process discussed in the above section, is crude 4,4'(5')-[di t-butyldibenzo]-18-crown-6, containing about 16% (GC) of 4,4'(5')-[di t-butyldibenzo]-18-crown-6. It is purified using chromatographic technique. Alumina column, loaded with the crude, is eluted with a solvent of optimum polarity (10% Ethyl Acetate in Petroleum Ether). Analysis of the different eluted fractions has revealed that the nature of elution is diffusive, accordingly a procedure consisting three consecutive column purification units have been developed. This process resulted in a purity of 86.4% (GC), and the yield of 4,4'(5')-[di t-butyldibenzo]-18-crown-6 was 10-12%, which is obtained as a white solid. This compound is also reported to be highly efficient in recovery of Tc from alkaline low level nuclear waste [5].

Synthesis of supported rhodium catalyst for hydrogenation reaction

Synthesis of 5% rhodium impregnated on γ-alumina support is carried out using microwave aided solvothermal reduction technique. Measured quantity of γ-alumina is impregnated with rhodium chloride (from aqueous solution RhCl₃); in a high temperature sonication bath. The impregnated alumina is dried under vacuum at 200°C followed by calcination at 300°C, for 6 hours. Rh[III] is then reduced to Rh[0], in a microwave reactor, using ethylene glycol under reflux condition. The change of colour from red to black gives an indication about the reduction. Activation of the catalyst is carried out at 300°C temperature under continuously purged hydrogen environment for 6 hours.

Characterisation of the synthesised catalyst

EDXRF (Xenematrix-EX 6600 SDD) analysis has shown that the surface has about 87.5% rhodium along with traces of zinc and iron as impurities. H₂ chemisorptions (Thermo Electron Corp.) studies have showed that the specific hydrogen coverage (BET) is in the range 89.69 – 118.2 m²/gm (Fig. 2.B). The nature of hysteresis in the isotherm (Fig. 2.A) shows the presence of uniform meso-pores.
Removal of moisture from the reactant and the reaction media of hydrogenation reaction

The reaction medium is n-butanol which is doubly distilled and is left to stand over molecular sieves (Sodium Alumino-silicate, 3Å, Finar). To enhance the polarity of the reaction media, valeric carboxylic acid is added to it [3]. It has comparatively long carbon chain (C5) which renders it to be hydrophobic in nature, thus it can be dried easily and stored without being attacked by moisture. Valeric acid is dried with anhydrous copper chloride, which is followed by vacuum distillation. DTBDB18C6 is dried by azeotropic distillation with benzene in a Dean-Stark collector [3].

Catalytic hydrogenation of 4,4'(5')-[di t-butyldibenzo]-18-crown-6

Catalytic hydrogenation of 4,4'(5')-[di t-butyldibenzo]-18-crown-6, has been carried out in autoclave of 50mL to 1 L capacity Stainless Steel (SS) 316 autoclaves. The ratio of the catalyst to the reactant is 1:5; the ratio of reactant to n-butanol was 1:10; the ratio of catalyst to valeric acid is 1:1. Temperature is maintained at 65°C, and pressure of hydrogen gas is maintained at 35-40 bar during the reaction. The reaction was allowed to take place for 40 hours. After which the reaction mixture is filtered to separate the catalyst. The solvent is removed through evaporation in vacuum. The product (now dark in colour) is dissolved in chloroform and passed through an alumina column, to remove washed out rhodium. After recovering chloroform from the eluted solution, the final product is obtained as a light coloured viscous liquid with 88% yield and 71.8% purity of desired product. The product is characterised by GCMS, FTIR and NMR analysis and found to be similar to the commercially available sample.

Figure 4.A shows the gas chromatogram peaks present in the hydrogenation product. It shows the presence of the hydrogenated product, DTBDCH18C6, the half hydrogenated product, (TBB)(TBCH)18C6 and traces of unreacted DTBDB18C6. Figure 4.B depicts the mass spectrum of DTBDCH18C6, with its mass peak (m/z) at 484. In figure 5.B, H1-NMR of the synthesized ligand, shows the disappearance of the peaks with proton shift of 6.8-7.265, and the presence of peaks with proton shift of 1.2-1.274. Thus, H1-NMR reveals that considerable amounts of phenyl group present in the reactant (Figure 5.A) have been hydrogenated. FTIR analysis of the synthesized ligand (Fig. 6) shows major peaks at 1098 cm\(^{-1}\), 2780 cm\(^{-1}\), 3310 cm\(^{-1}\) for C-O, C=O and O-H respectively, similar to that reported in literature for DTBDB18C6 [6].
Fig. 4: GCMS analysis of the product (A) Gas chromatogram of hydrogenation product; (B) Mass spectrum of 4,4'(5')-[di t-butylidicyclohexano]-18-crown-6
Fig. 5: H$^1$ NMR analysis, (A) Reactant, (B) Product

Fig. 6: FTIR analysis of synthesized ligand
Effect of the composition of the reaction medium

The reaction is extremely sensitive towards the presence of moisture in reaction media, which prevents the reaction to take place. The presence of valeric acid in the reaction media has an enhancing effect on the yield and chemo-selectivity of the hydrogenation reaction which has been illustrated in Fig. 7. In absence of valeric acid, catalytic hydrogenation mostly yields the half hydrogenated crown ether, (TBB)(TBCH)18C6 i.e., B in Fig. 3; which results in a distribution coefficient of 1.7 for strontium in 4N nitric acid solution, with 0.2M solution in octanol. On contrast, in presence of valeric acid the reaction proceeds to DTBDCH18C6 i.e., C in Fig. 3, which is the major product. The distribution coefficient of Strontium with this product was found to be about 13.6 under similar conditions. The most probable explanation to this observation may be that valeric acid enhances the polarity of the reaction media, which in turn increases the solubility of hydrogen in the reaction media.

Evaluation of synthesised 4,4'(5')-[di t-butylidicyclohexano]-18-crown-6

The synthesised compound was tested for its ability to extract strontium from acidic solution. It is dissolved in organic diluents and contacted with 30-45 ppm Strontium in 4M nitric acid, for 10 mins. The distribution coefficient of strontium, for various diluents is depicted in Fig. 8. The product was found to be soluble in conventional solvents, like dodecane, isodecanol, octanol etc. The maximum distribution coefficient of 22.47 was obtained with 0.2M solution of the synthesised ligand in 1:1 mixture of dodecane and isodecanol with pure strontium nitrate feed solution. 85-90% stripping was obtained, with three contacts of Demineralised Water (DM).

Distribution coefficient for Sr, Am, Pu, Cs in simulated radioactive waste was found to be about 7.26, 0.01, 0.26, and 0.1 respectively. These experiments were carried out with 0.1M DTBDCH18C6 in octanol, in Waste Immobilisation Plant (WIP) Lab, Mumbai. Accordingly, the selectivity for strontium was found to be greater than 48.
Conclusion

4,4'(5')-[di t-butyldicyclohexano]-18-crown-6 was synthesised in batches ranging from 3- 43 grams in 50 mL to 1L SS autoclave. NMR, GCMS and FTIR characterisation identifies the synthesised ligand as 4,4'(5')-[di t-butyldicyclohexano]-18-crown-6. The hydrogenation reaction is found to be sensitive to the polarity of the medium which is enhanced by presence of C5 carboxylic acid. The synthesised 4,4'(5')-[di t-butyldicyclohexano]-18-crown-6 is found to have high distribution coefficient and high selectivity (>45) for strontium w.r.t. impurities like americium, plutonium, cesium etc present in acidic high level nuclear waste. The precursor 4,4'(5')-[di t-butyldicyclohexano]-18-crown-6 was synthesised in 400 gm batch with about 86% purity and 10% yield.

References


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Abbreviations

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCH18C6</td>
<td>Dicyclohexano-18-crown-6</td>
</tr>
<tr>
<td>DD</td>
<td>Dodecane</td>
</tr>
<tr>
<td>ID</td>
<td>Isodecanol</td>
</tr>
<tr>
<td>TBP</td>
<td>Tri-n-butyl phosphate</td>
</tr>
</tbody>
</table>
बिजली की आवश्यकता का अनुमान लगाना
अभी हमें चर्चा करना है कि "भारत को कितनी बिजली की आवश्यकता है।" इसका जवाब देने के लिए हमें टॉप-डाउन अर्थव्यवस्थी मौलत के अनुसार, हमें अर्थव्यवस्था में बढ़ती हुई जिला, आर्थिक वृद्धि और उन्नत आर्थिक वृद्धि के बीच के संबंध तथा ग्रामीणों के विभिन्न अनुभवों को जोड़ते हुए विश्लेषण करना पड़ेगा। जैविक वातावरण के अनुसार, हमें उपयोग की आवश्यकता, बजार और उपयोग के आधार पर बिजली की मांग का अनुमान लगाना होगा। इस प्रकार, पूर्वशतुरा के लिए कई दायित्वों का प्रयोग किया जाता है जिनका वातावरण वैज्ञानिक संस्करण से जुड़े समय साथ भी जोड़ा गया है। इस प्रकार, वैज्ञानिक उन्नति दर में उन्नत जीवन दर में बढ़ती गई है। इस तथ्य से संबंधित विषयों की जानकारी मिल सकती है।

बिजली का उपयोग बनाने के लिए, एक सरल विश्लेषण है। हमारी आपसी बातचीत में मिला गया है। ऐसा माना जा सकता है कि 2050 के लिए अनुमान और वातावरण 2016-17 में कुल उपयोग का बहुत उल्लिखित है और विभिन्न उपयोग के माध्यम से यह अनुमान लगाया गया है। इस्तेमाल के लिए विशेष आवश्यकता या उपयोग के माध्यम से ध्यान देना चाहिए।

महत्वपूर्ण बिजली उपयोग के लिए निर्धारण करना उपयोग के लिए उत्पादन की उन्नति के लिए एक बड़य संपर्क के लिए विभिन्न उपयोग के माध्यम से हमारी आवश्यकता का अनुमान लगाना होगा। यह विश्लेषण के प्रति विभिन्न उपयोग के माध्यम से हमारी आवश्यकता का अनुमान लगाना होगा। इस तथ्य से संबंधित विषयों की जानकारी मिल सकती है।
Article

BARC Newsletter | May-June 2017 | 27

The present research highlights the importance of various factors in the context of nuclear reactor design and operation. It emphasizes the role of material properties and their impact on the reactor's performance. The study also discusses the challenges associated with nuclear safety and the ongoing efforts to enhance reactor technologies.

The article further delves into the advancements in reactor technology, focusing on the integration of emerging technologies and their potential implications. It also highlights the importance of interdisciplinary collaboration in addressing the complex issues related to nuclear energy.

The research concludes with an outlook on future directions and the need for continued innovation to meet the growing demands for sustainable energy solutions. It underscores the importance of collaborative efforts between researchers, policymakers, and industry stakeholders to ensure a safe and efficient nuclear energy future.

Overall, the article provides a comprehensive overview of the current state of nuclear reactor technology, emphasizing the need for continuous research and development to overcome the existing challenges and pave the way for future innovations.
बालक लाभयोग्य लोगों में बिना उत्पन्न होने वाले आक्सीमुस एवं केरियोनिया, यूप्रेग आक्सीमुस बहुत संभव है जब भी आक्सीमुस संबंधित है। जब आक्सीमुस अभाव होता है, तो लाभयोग्य लोगों के लिए आक्सीमुस संबंधित है। अवस्थिति के अंतर्गत लाभयोग्य लोगों के लिए आक्सीमुस संबंधित है। आक्सीमुस के लिए आक्सीमुस संबंधित है। आक्सीमुस के लिए आक्सीमुस संबंधित है।
BARC celebrates the National Technology Day (NTD) on May 11 to mark India’s advancements in technology. Dr. S. Christopher, Chairman, Defence Research and Development Organisation (DRDO) and Secretary, Department of Defence Research & Development was the chief guest for the event. In the inaugural session, Shri K. N. Vyas, Director, BARC welcomed the chief guest and Dr. Sekhar Basu, Chairman, Atomic Energy Commission delivered the presidential address. Shri B. S. Jagadeesh, Associate Director, Electronics & Instrumentation Group (E&IG) and Head, Computer Division explained the significance of the National Technology Day to the audience. In his keynote address titled “Innovation – AEWACS programme: A Case Study” Dr. Christopher highlighted various innovations by the design team of the Airborne Early Warning and Control System in DRDO. Shri R. S. Mundada, formerly Associate Director E&IG and Convenor NTD - 2017 proposed the vote of thanks.

BARC organises a technological exhibition based on a certain theme to mark the National Technology Day. This year’s theme is “Electronics and Computer Technology – Empowering the Nation”. The chief guest inaugurated the exhibition in the Central Complex auditorium, which showcased exhibits and posters on various technologies and systems developed in BARC. The exhibition was visited by about 1000 students from different schools across Mumbai during May 11-14, 2017.

In the later part of the day, a technical session comprising of talks by the recipients of the Homi Bhabha Science and Technology Awards, 2015 was organised in the Supercomputing Facility auditorium. Dr. R. Mittal, Solid State Physics Division, BARC, Dr. A. K. Chaturvedi, Atomic Minerals Directorate for Exploration and Research, Dr. P. K. Mukherjee, Nuclear Agriculture and Bio-Technology Division, BARC, Dr. John Philip, Indira Gandhi Centre for Atomic Research and Shri S. B. Patil, Technology Development Division, BARC made their award winning presentations.

Further, BARC also arranged an exhibition in the DAE convention centre, Anushakti Nagar during May 13-14 for the benefit of the general public. Shri S. A. Bharadwaj, Chairman, Atomic Energy Regulatory Board inaugurated the exhibition. Infotainment shows and skits were staged to make it more interesting for the visitors here.

Dr. S. Christopher, Chairman DRDO and Secretary, Dept. of Defence R&D, delivering the keynote address
Inauguration of the exhibition on May 11

The Chief Guest at the exhibition on May 11

Inauguration of the exhibition on May 13

The Chief Guest at the exhibition on May 13

Visitors at the exhibition on May 13-14

Visitors at the exhibition on May 13-14
Central Complex at BARC