

SIMULTANEOUS LSC MEASUREMENT OF $K_3^{60}Co(CN)_6$ AND $^{114m}InEDTA$ TRACERS IN GROUNDWATER

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ABSTRACT. We describe a method for determining $^{114m}InEDTA$ and $K_3^{60}Co(CN)_6$ in water samples by chemical separation followed by liquid scintillation counting (LSC). These radioisotope-labeled compounds are used as tracers for underground and surface waters. In multitracers field experiments, both tracers can be determined simultaneously in double-labeled samples. Detection limits obtained by a low-background Quantulus 1220TM LS spectrometer, using 1-liter water samples and 100 min counting time, are 4 Bq m^{-3} and 12 Bq m^{-3} for $^{114m}InEDTA$ and $K_3^{60}Co(CN)_6$, respectively. We also describe field applications.

INTRODUCTION

In spite of the increasing application of natural isotopes in hydrological investigations, artificial radioisotopes are still being used as well. A main advantage of using artificial radioisotopes for water tracing is their absence in the natural environment. They are particularly useful when the natural isotopes are virtually invariant and other tracers, such as dyes, cannot be employed because waters can be highly polluted. In such cases, 3H -labeled water is sometimes used. However, artificial 3H precludes any future applications of natural 3H in the investigated zone. Thus, we avoid its use. We describe here our study that involves other artificial radioactive tracers, $K_3^{60}Co(CN)_6$ (Sternau 1967; Zuber, Turek & Maloszewski 1976) and $^{114m}InEDTA$ (Hanson 1970; Lebecka & Tomza 1977), which are very stable in a water-rock environment. For radiation safety, as well as economic reasons, it is always essential to keep detection limits of tracers to a minimum. In multitracers experiments, it is also important to determine tracers in double-labeled water samples. One can achieve very low detection limits of beta-emitting tracers by using low-background liquid scintillation (LS) spectrometers.

METHODS

We chose $^{114m}InEDTA$ and $K_3^{60}Co(CN)_6$ because they are transported easily in water-rock environments, and the half-lives of ^{114m}In (50 d) and ^{60}Co (5.3 yr) enable applications in medium- and long-term field experiments. The stability constant of $InEDTA$ is $\log K = 25$. Its performance in water-rock environments has been noted in numerous laboratory and field experiments (Behrens, Moser & Wildner 1977; Lebecka & Tomza 1977). The stability of $K_3Co(CN)_6$ is even higher ($pK = 64$), which enables the tracer to be transported by groundwater with almost no losses or delays (Sternau *et al.* 1967; Zuber, Turek & Maloszewski 1976; Lebecka, Tomza & Trzebicka 1985). These tracers can be used simultaneously in multitracers experiments because they can be determined simultaneously in double-labeled water samples.

Our analytical procedure consists of chemical separation of tracers, followed by measurement in a Quantulus 1220TM low-background LS spectrometer, which has both passive and active guard. Because the chemical separation of tracers was not quite complete, we made corrections using spectrum analysis and the differences of the half-lives of ^{114m}In and ^{60}Co . We performed chemical separation by dividing the 2-dm^3 water sample into two equal parts. Figures 1 and 2 show our preparation procedure.

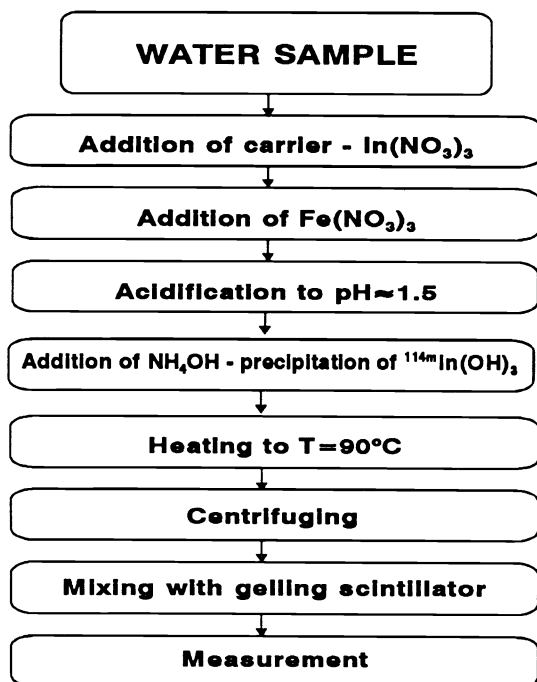


Fig. 1. Preparation of $^{114m}\text{InEDTA}$

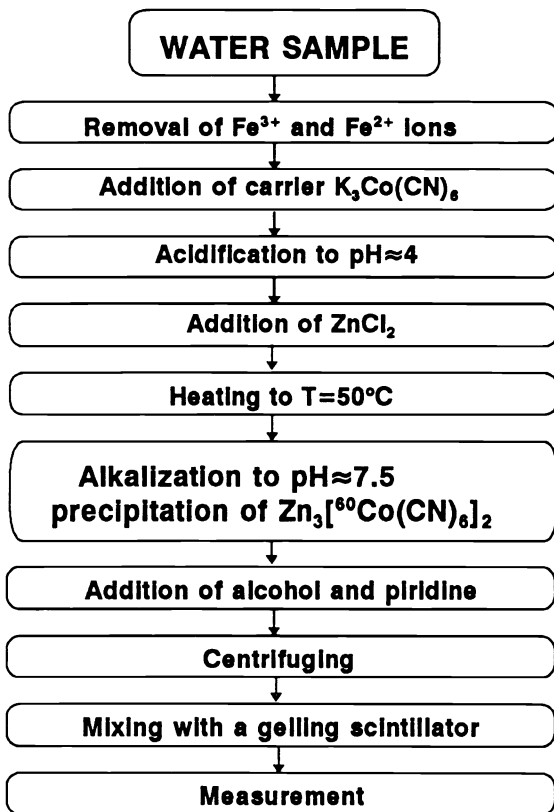


Fig. 2. Preparation of $\text{K}_3^{60}\text{Co}(\text{CN})_6$

^{114m}In can be measured only after released from EDTA. This is done by substituting In^{3+} with Fe^{3+} in the EDTA complex at pH below 1. Then ^{114m}In is co-precipitated with non-radioactive In carrier as hydroxide. The indium hydroxide precipitate is mixed with water and gelling scintillator. ^{60}Co present in the initial sample as $\text{K}_3^{60}\text{Co}(\text{CN})_6$ remains in the solution. The separation is rather good; nevertheless, occluded traces of ^{60}Co are often present in the precipitate. After the first precipitation, *ca.* 5% of ^{60}Co may remain in the precipitate. Results of the latter operation are much improved when it is repeated and the precipitate is almost free of ^{60}Co (below 1%). However, for practical reasons, precipitation is usually not repeated, because satisfactory results can be obtained by using differences in spectra and half-lives.

For chemical separation of ^{60}Co , the $\text{Co}(\text{CN})_6^{3-}$ anion is precipitated from solution by Zn^{2+} ions. Because solubility of the $\text{Zn}_3[\text{Co}(\text{CN})_6]_2$ is rather high, a sufficient amount of carrier (the amount of $\text{K}_3\text{Co}(\text{CN})_6$ carrier must correspond to at least 20 mg of Co^{3+} liter $^{-1}$) must be added to obtain a satisfactory reaction yield (~96%). A better yield, even with a smaller amount of carrier, was achieved using Pb^{2+} instead of Zn^{2+} , but the Pb precipitate was very heavy, which caused poor detection efficiency due to gel instability and quenching. The addition of alcohol and piridine improves the reaction yield. To avoid dissolution of precipitate and loss of tracers, the precipitate is rinsed in alcohol. Unfortunately, the precipitate contains up to 40% (by activity) of ^{114m}In present in the initial sample. This can be reduced by repeating the precipitation, if needed. As in the case of $^{114m}\text{InEDTA}$, this is usually not done in practice. The precipitate is then mixed with water and gelling scintillator.

Figure 3 shows the spectra of single-labeled samples after chemical preparation measured by the Quantulus 1220TM. One spectrum belongs to a sample labeled with ^{114m}In . Because of the counting conversion electrons of ^{114m}In (162–189 keV) and β particles emitted by ^{114m}In ($E_{\beta\text{max}} = 1.988$ MeV), as well as very low background, a lower limit of detection (LLD) of 4 Bq m $^{-3}$ can be achieved (100-min counting time). This is about four times lower than the detection limit obtained using a Rackbeta 2 LS spectrometer (Lebecka, Tomza & Trzebicka 1985). The annual limit of intake (ALI) for ^{114m}In is 2×10^5 Bq. Thus, ALI corresponds to 50,000 m 3 of water, with a concentration of ^{114m}In equal to detection limit.

The second spectrum in Figure 3 belongs to a sample labeled with ^{60}Co , where β particles ($E_{\text{max}} = 0.310$ MeV) and Compton electrons created by gamma rays of ^{60}Co ($E_\gamma = 1.17$ and 1.33 MeV) are counted. We obtained an LLD of $\text{K}_3^{60}\text{Co}(\text{CN})_6$ equal to 12 Bq m $^{-3}$ using a 1-liter water sample (100 min counting time). This is about five times lower than results obtained by using a Rackbeta

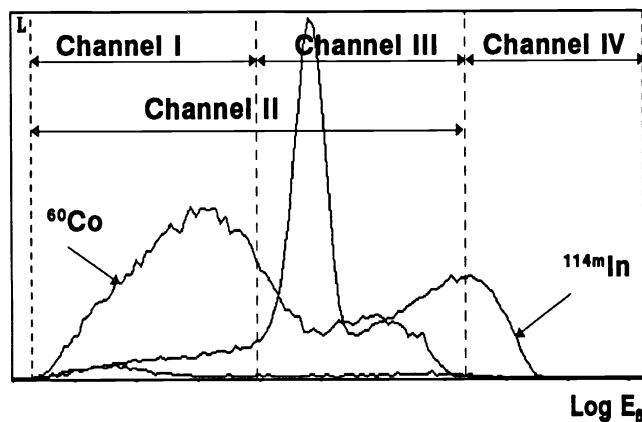


Fig. 3. Spectra of ^{114m}In and ^{60}Co

2 LS counter (Lebecka, Tomza & Trzebiecka 1985). The achieved LLD enables detection of $K_3^{60}\text{Co}(\text{CN})_6$ in a concentration of 2×10^{-6} ALI per 1 m^3 .

We obtained the LLD presented above for single-labeled samples, but even though tracers were chemically separated, separation was incomplete. Thus, additional steps were required. With double-labeled samples, the interpretation of measurements can be done by two methods:

1. *Differences in spectra*: for double-labeled samples, the activity of $^{114\text{m}}\text{In}$ and ^{60}Co can be calculated by computer analysis of spectra in comparison with spectra of single-labeled samples. It can also be done very simply as follows. In the high-energy part of the spectrum (Fig. 3, channel IV) only β particles emitted by $^{114\text{m}}\text{In}$ are registered. Thus, the number of counts in this channel can be used for measuring $^{114\text{m}}\text{InEDTA}$. On the basis of the count rate in channel IV, the count rate resulting from $^{114\text{m}}\text{In}$ in channel I can be calculated from the spectrum of a single-labeled sample. The difference between the total count rate in channel I and the calculated value gives the count rate resulting from the presence of ^{60}Co .
2. *Differences in half-lives*: the measurements are performed twice in time periods sufficient to allow significant decay of $^{114\text{m}}\text{In}$ (at least two weeks). In this case, counting was done in channels with good counting efficiency (channel II for ^{60}Co and channel III for $^{114\text{m}}\text{In}$, Fig. 3). Results obtained by spectral analysis and by using decay constant differences were evaluated and the final result calculated. For double-labeled water samples, the detection limits for both tracers were several times higher than for single-labeled samples. Nevertheless, LLDs were still very good compared to other radioactive tracers.

RESULTS AND DISCUSSION

Artificial radioactive tracers used in hydrology are measured usually by γ detectors, mostly by NaI(Tl). The main advantage of γ -detection is simplicity and the possibility of performing *in-situ* measurements. The best LLDs by this technique were obtained by Zuber, Turek and Maloszewski (1976) for $K_3^{60}\text{Co}(\text{CN})_6$ (the LLD for infinite geometry was 185 Bq m^{-3}) and by Moser (1967) for $K^{131}\text{I}$. Moser separated the tracer by precipitation from 1-m^3 water samples and obtained LLD 166 Bq m^{-3} . In comparison, the LLD obtained by LSC, 4 Bq m^{-3} for $^{114\text{m}}\text{InEDTA}$ and 12 Bq m^{-3} for $K_3^{60}\text{Co}(\text{CN})_6$, are much better, even for double-labeled samples. Tracer measurements can be applied to natural waters with high salinity and high levels of natural radiation.

APPLICATIONS

Tracers have been used singly and in multitracer experiments. $^{114\text{m}}\text{InEDTA}$ was used for measuring water balance in a coal mine in Upper Silesia, where underground abandoned workings were used as a settling pond for wastewaters from a coal processing plant. Both natural waters and wastewaters flowed into this settling pond. The total volume of the water reservoir was $\sim 46,000 \text{ m}^3$; 37 MBq of $^{114\text{m}}\text{In}$ was used. The experiment lasted about two months. During this time, we were able to determine the residence time and balance of wastewaters, which indicated that the settling pond was not growing, and thus, was no threat to the underground mine. Measurements were achieved despite difficulties such as a high mineral content of the water ($\sim 4.5 \text{ g dm}^{-3}$) and the presence of coal slime.

In another experiment, both tracers were used simultaneously for investigating the hydrological conditions in the iron ore bed to drain the strata overlying the ore bed (Fig. 4). The tracers were injected into two piezometers. The well situated between these piezometers was pumped and sampled. Simultaneous determination of $^{114\text{m}}\text{InEDTA}$ and $K_3^{60}\text{Co}(\text{CN})_6$ was performed. Based on

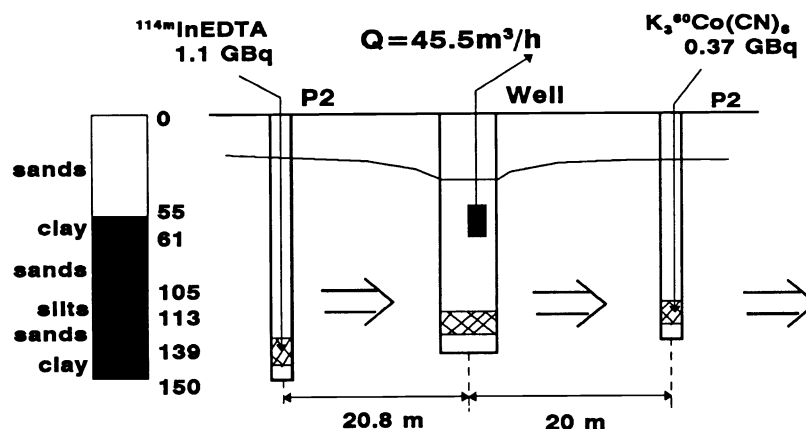


Fig. 4. Multitracer experiment

the transit curves of the tracers, we determined the permeability of different strata and the real (distance) velocity of water, effective porosity and filtration coefficient under natural conditions. Because the tracers were introduced into different aquiferous layers, the hydraulic connections between these layers could also be confirmed.

CONCLUSIONS

We have developed a method for determining $^{114m}\text{InEDTA}$ and $\text{K}_3^{60}\text{Co(CN)}_6$ in water samples, which enables us to measure these artificial radioisotopes in very low concentrations, particularly with a low-background LS spectrometer. The tracers can be used in field investigations, as their good detectabilities require only small amounts of tracers. Measurement is simple, and an additional advantage is the possibility of using the tracers in saline water and in water with high natural radioactivity.

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