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Comparative study of two drying techniques used in radioactive source preparation: Freeze-drying and evaporation using hot dry nitrogen jets

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Abstract

Quantitative solid sources are used widely in the field of radionuclide metrology. With the aim to improve the detection efficiency for electrons and x-rays, a comparative study between two source drying techniques has been undertaken at LNE-Laboratoire National Henri Becquerel (LNE-LNHB, France). In this paper, freeze-drying using commercial equipment is compared with a system of drying using hot jets of nitrogen developed at Institute for Reference Materials and Measurements (IRMM, Belgium). In order to characterize the influence of self-absorption, the detection efficiencies for ^{51}Cr sources have been measured by coincidence counting and photon spectrometry.
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1. Introduction

In the field of radionuclide metrology, solid radioactive sources are used for various measurement methods such as coincidence counting or photon spectrometry. When preparing such solid radioactive sources, it is important to use a drying process that both minimizes the source self-absorption and optimizes the radioactive residual homogeneity. For that purpose, a comparative study between the two alternative techniques has been undertaken at LNE-Laboratoire National Henri Becquerel (LNE-LNHB, France). The results described have been obtained in the framework of participation in the Système International de Référence (SIR) concerning ^{51}Cr in 2006 (Ratel and Michotte, 2003). Indeed, due to the low-energy electrons and x-rays emitted, this radionuclide is particularly well-adapted in the characterization of self-absorption in dry sources.

Evaporation at atmospheric pressure is the usual drying process in the preparation of radioactive sources. In this paper, the first alternative technique, based on freeze-drying, is described. Using commercial equipment, this technique has

been implemented at LNE-LNHB for several years. Previous work showed a significant improvement in source homogeneity and in detection efficiencies (de Sanoit et al., 2004), confirming results obtained in the past (Patte and Yaffe, 1956; Baerg and Bowes, 1971). The other alternative technique is based on a source dryer developed at the Institute for Reference Materials and Measurements (IRMM, Belgium); in this case, the drying process is performed using nitrogen jets at elevated temperature (Denecke et al., 2000).

For the two techniques, the detection efficiencies obtained by coincidence counting and photon spectrometry are given as functions of the deposited source mass. The homogeneity of the radioactive sources was checked by autoradiography, and the carrier concentration of the standard solution was investigated to assure thermodynamic stability of the radioactive solution and minimization of self-absorption in the dry sources.

2. Experimental techniques

2.1. Preparation of the standard solution of ^{51}Cr

The chemical composition (carrier concentration and oxidation state of chromium) of the standard ^{51}Cr solution

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was investigated to optimize the thermodynamic stability, and was changed from that used in the sources prepared for the two SIR submissions of LNE-LNHB in 1984 and 1994 (Ratel and Michotte, 2003; Ratel et al., 2005). In both cases, the coincidence method was used to measure dry sources. Unlike the SIR submission in 1994, the standardization in 1984 was revealed to be non-consistent with the SIR reference value (Ratel et al., 2005). This discrepancy could have been due to the chemical composition. In 1984, the standard solution had a $CrCl_2$ carrier concentration equal to $10\,\mu g\,g^{-1}$ in 0.1 M HCl, which was later considered too low. Moreover, the oxidation state of chromium (II) is not stable in solution (Charlot, 1983). As a consequence, the oxidation state of chromium (III) had been chosen for the 1994 submission, and the carrier concentration was increased to $100\,\mu g\,g^{-1}$ in 0.1 M HCl [corresponding to $33\,\mu g\,g^{-1}$ of Cr (III)].

For the SIR submission in 2006 and in the present study, the oxidation state of chromium (III) has been maintained. Because chromium chloride salts are deliquescent, the hexa-hydrated form has been used. The carrier concentration of $CrCl_3 \cdot 6H_2O$ was minimized in order to reduce self-absorption of the dry sources, but kept sufficiently high for the stability of the standard ^{51}Cr solution. Consequently, the carrier concentration was fixed to $100\,\mu g\,g^{-1}$ in 0.1 M HCl, corresponding to $20\,\mu g\,g^{-1}$ of Cr(III) (Iroulart, 2006a). The activity concentration was approximately $3\,MBq\,g^{-1}$.

The adsorption of radioactive ions in solution on the inner surface of glassware is a well-known problem. At LNE-LNHB, a routine procedure has been established to minimize this problem (Iroulart, 2006b, 2007). Laboratoryware was filled with a carrier solution of $100\,\mu g\,g^{-1}$ $CrCl_3$ $6H_2O$ in 0.1 M HCl and was emptied after 24 h and dried in an oven.

Impurity checks of the standard solution were carried out by γ- and x-ray spectrometry.

2.2. Source preparation

For coincidence counting and photon spectrometry, sources were prepared on gold-coated VYNS® foils mounted on a stainless-steel ring (de Sanoit et al., 2004). A mixture consisting of a seeding agent (latex microspheres; Estapor® K-007, Aldrich) and a wetting agent (Tween® 20, Aldrich) in ethanol was previously electrosprayed on the foil (Blanchis et al., 1990) as a disc-shaped deposit of 9 mm diameter. All sources were prepared, using the pycnometer technique, by depositing a weighed drop of the standard solution of ^{51}Cr (masses ranging from 6 to 30 mg).

Two different batches of freeze-dried sources were prepared at different times: 11 for coincidence counting and 5 for photon spectrometry. Two different batches were also prepared using the IRMM source dryer at different times: 10 for coincidence counting and 6 for photon spectrometry.

Dry sources were stored in a desiccator in order to limit rehydration.

2.3. Freeze-drying

Freeze-drying can be described as a dehydration process (Franks, 1998) operating by sublimation under reduced pressure of a frozen product (in our case corresponding to the radioactive deposit). Contrary to the usual drying procedures like evaporation under atmospheric pressure, freeze-drying prevents significant changes in source shape during the drying process. As a result, no crown-shaped radioactive sources are observed (de Sanoit et al., 2004). Moreover, during the first freezing step, the literature usually reports that rapid cooling leads to a fine crystalline structure (Bruttini et al., 1991).

In the case of diluted solutions, as described in the literature, at the end of the first freezing step, a separation occurs leading to a frozen product (consisting of the aqueous component of the radioactive solution) and to an unfrozen material, which is, in our case, a highly concentrated mixture containing carrier and radioactive salts. During the consecutive sublimation stage, the behavior of the unfrozen material is rather complex (Franks and Murase, 1992; Roos, 1997). Indeed, depending on the solution components, different mechanisms related to the temperature are possible: crystallization at eutectic temperature, glass transition, and formation of a supersaturated mixture.

At LNE-LNHB, freeze-drying is implemented using a commercial apparatus (Christ® Alpha 2–4), already described in a previous work (de Sanoit et al., 2004); it consists of a low-pressure chamber comprising an ice condenser operating at $-85\,°C$. The temperature and the pressure inside the chamber are the only parameters controlled during the freeze-drying process. After sources are prepared as described above, they are placed on a source tray inside the chamber and the vacuum pump is started immediately. Contrary to the previous work (de Sanoit et al., 2004), no pre-cooling step is applied at atmospheric pressure, allowing a significant decrease in the time to freeze the sources (roughly less than 1 min) depending on the deposited drop mass and the drop spreading. The cooling and subsequent freezing of the radioactive deposit are due to self-evaporation under reduced pressure. The chamber pressure has to be controlled in order to avoid bubble formation and obtain a stable evaporation process (Satoh et al., 2002).

The chamber pressure is lowered to 1 Pa during the sublimation phase to obtain a complete solidification of the unfrozen mixture. The main drawback is the long duration of the sublimation phase, which generally exceeds 1 h corresponding to the complete removal of the frozen aqueous component. The additional experiments carried out after the present study have shown that sublimation duration can be significantly reduced (to under 20 min) when operating at higher pressure (around 30 Pa); in the

literature, this corresponds to the primary drying step (Dern, 2005). The chamber pressure is lowered afterwards to 1 Pa in order to optimize solidification and desorption (Rey, 1999).

Finally, nitrogen gas is introduced inside the chamber to prevent source rehydration while the atmospheric pressure and the ambient temperature are recovered. However, precautions have to be taken because water vapor condensation on sources cannot be completely prevented; the consequence is the production of radioactivity homogeneity defects on sources, which can be visualized by autoradiography. This condensation effect is clearly seen on the source tray and has to be avoided in future. For the present study, the total time needed for freeze-drying the drop-deposited sources was about 3 h.

2.4. Drying with hot-nitrogen jets

Willie et al. (1970) showed that the homogeneity of a radioactive source can be improved by agitating the deposited drop with a jet of heated, dry nitrogen as compared to conventional drying. Denecke et al. (2000) developed a source dryer based on this technique. By accelerating the drying process, the formation of large crystals is prevented. A source dryer, developed and produced at IRMM, was purchased by LNE-LNHB and used for the present comparative study.

The following drying procedure has been applied: the source is laid on a source tray, which is placed on a turntable; in order to obtain a symmetrical profile of the radioactive deposit, the rotation speed is set at around 100 rpm.

The drying process is performed at reduced pressure equal to about 1.2×10^4 Pa (the whole system is hermetically closed by a transparent bell jar). With the temperature set at around 70 °C, four nitrogen jets (diametrically opposite) provide a flow of 3–4 L min^{-1} with an adjustable distance between 1 and 3 cm from the source. During the process, the nitrogen jets are moved from the periphery to the center of the radioactive deposit until drying is complete. This procedure prevents projections of radioactive solution outside the disc-shaped spot of latex microspheres. Sources with a mass of 30 mg can be dried in about 10 min.

3. Results and discussion

3.1. Source homogeneity check

The homogeneity of the dry radioactive sources was checked by digital autoradiography using the BAS-1800 II® Storage Phosphor Imaging System and a photostimulable phosphor plate (Amemiya and Miyahara, 1988). As depicted in Fig. 1, the autoradiographs reveal three main types of source profiles: satisfactory homogeneity profiles without homogeneity defects in the radioactive deposit (type A), profiles including homogeneity defects in the radioactive deposit (type B) and crown-shaped profiles with possible homogeneity defects (type C).

In the case of the freeze-dried coincidence sources, as expected, no crown-shaped profiles were obtained. However, due to condensation at the end of the freeze-drying process, two sources presented type B profiles. No significant problems were encountered in the preparation of the freeze-dried sources dedicated to photon spectrometry, only satisfactory type A profiles were obtained.

For sources prepared with the nitrogen-jet system, seven of the coincidence sources presented crown-shaped profiles (type C). This problem is not mentioned by Denecke et al. (2000) and could be due to the lack of practice at LNE-LNHB. In contrast, this problem was not encountered in the case of the sources prepared for photon spectrometry, although there was some indication that radioactivity was more concentrated in the center (perhaps due to an inaccurate orientation of the nitrogen jets during the drying process).

3.2. Coincidence measurements

The coincidence method is widely implemented in National Metrology Institutes (NMIs) as a particularly well-adapted method to the standardization of a large variety of radionuclides decaying through two or more radiations (Campion, 1959). At LNE-LNHB, this technique is applied using a live-timed anti-coincidence system based on home-made electronic modules (Bouchard, 2000, 2002).

^{51}Cr disintegrates through electron capture to ^{51}V; the subsequent emission consists largely of low-energy electrons (below 5.5 keV). As a consequence, the detection efficiency of the dry sources in a proportional counter depends on the absorption of the electrons in the sources. In the case of simple decay-scheme radionuclides such as ^{51}Cr, the detection efficiency can be directly measured using the N_c/N_γ ratio between the coincidence (N_c) and the γ-(N_γ) count rates. In order to characterize the self-absorption influence, this value is later correlated to the deposited mass. The detection system is composed of a pill-box-type proportional counter in the β-channel (filled with Ar(90%)–CH$_4$(10%) at atmospheric pressure) and a HPGe detector in the γ-channel. The N_c/N_γ ratio is measured using a γ-window centered on the 320 keV energy peak of ^{51}Cr.

Fig. 2 displays the N_c/N_γ ratios obtained for the two drying techniques according to the deposited masses. At first glance, two mass groups can be distinguished. Indeed, for masses lower than 12 mg, a correlation between the N_c/N_γ ratios and the deposited masses can be observed. However, source non-homogeneities seem to have no significant influence in this case. For mass values above 12 mg, the interpretation of the results is more difficult. The N_c/N_γ ratios present a large variability and no correlation arises with the deposited masses. The highest detection efficiencies correspond to the freeze-dried sources for which
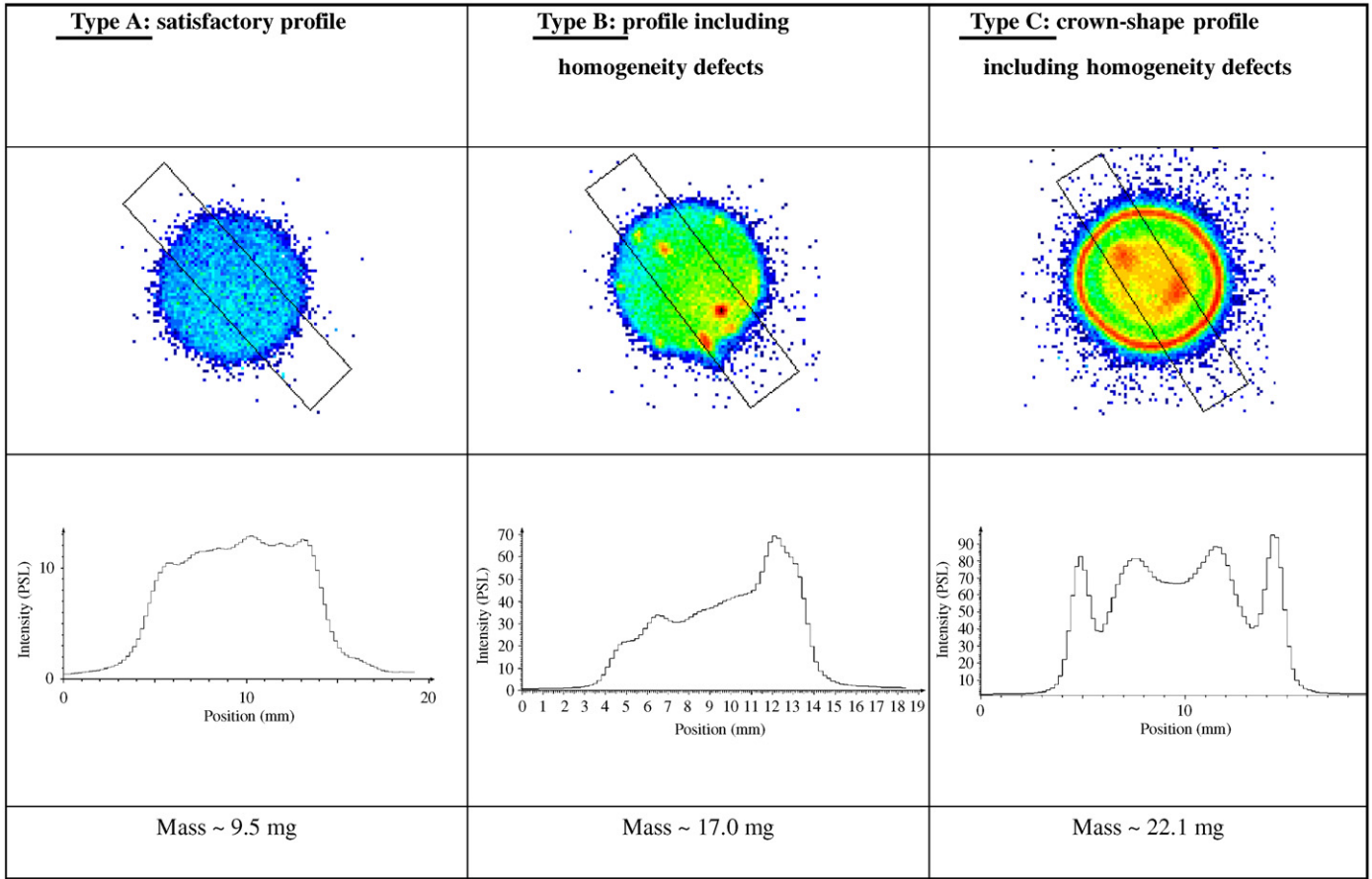
Type A: satisfactory profile	Type B: profile including homogeneity defects	Type C: crown-shape profile including homogeneity defects
Mass ~ 9.5 mg	Mass ~ 17.0 mg	Mass ~ 22.1 mg

Fig. 1. Autoradiographs and radioactivity profiles obtained from ^{51}Cr solid sources. The profiles can be classified according to three types. No crown-shaped profiles were observed in freeze-dried sources. Zones of high-activity concentration are indicated by red.
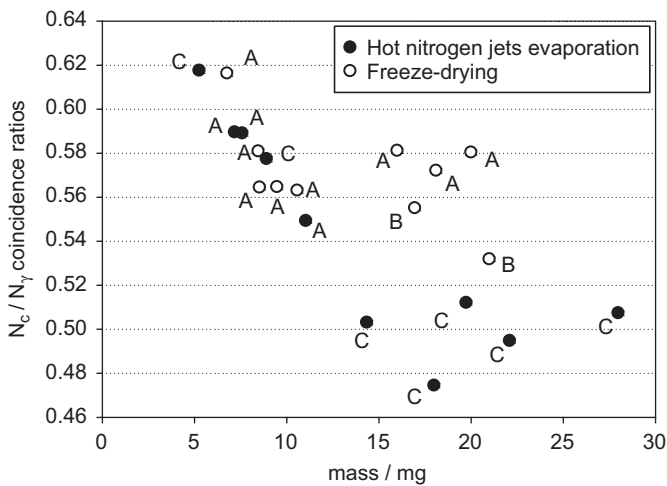

Fig. 2. Detection efficiencies N_c/N_γ from coincidence counting of ^{51}Cr solid sources as a function of deposited masses. The profile type for each source is also indicated. The freeze-dried sources and the sources dried with the IRMM source dryer are, respectively, symbolized by white and black spots.

the two lowest values present homogeneity defects (type B profile). The lowest detection efficiencies correspond to the sources dried with the IRMM system, but these sources

have significant non-homogeneities (crown-shaped type C profiles).

3.3. Photon spectrometry measurements

As ^{51}Cr emits both low-energy V K x-rays (4.9 and 5.4 keV) and a gamma ray of 320.1 keV, the relevant emerging photon flux has been measured using two semiconductor detectors (a silicon–lithium, Si(Li), detector and a high-purity germanium, HPGe, detector, respectively).

For each measurement, the source position is accurately checked using an optical microscope. Quantities of interest are the full-energy peak (FEP) areas, the single 320 keV peak for the HPGe detector and the Kα–Kβ doublet for the Si(Li). Net peak areas are obtained by subtracting a linear background using the same regions of interest. For each measurement, the acquisition time is adjusted to obtain at least 2×10^5 counts in the FEP. Assuming a negligible self-absorption for the 320 keV photons, the FEP counting rates recorded with the HPGe detector have been taken as a reference of the source activity. The counting rates of the FEP observed with the Si(Li) detector are thus normalized by gamma counting.

Fig. 3 displays the Si(Li)-to-HPGe counting ratios versus the source masses. Firstly, a satisfactory result is that no
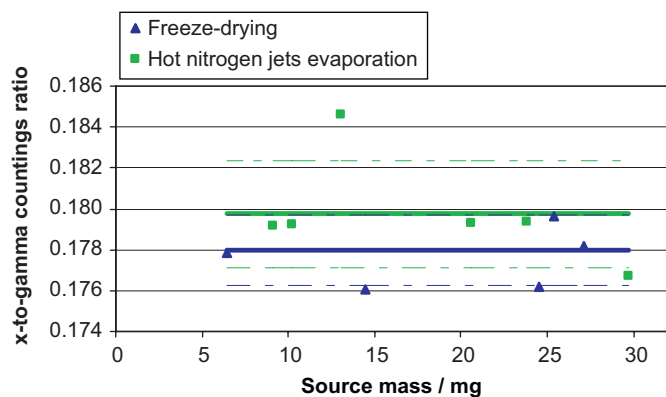
Fig. 3. X-to-γ counting ratios of ^{51}Cr solid sources dried by freeze-drying and by evaporation using hot-nitrogen jets. The individual ratio for each source is displayed as a function of the source mass. For each drying method, the mean value and the associated standard deviation are also drawn as solid and dotted lines, respectively.

influence of the source masses can be distinguished. Secondly, the mean counting ratio for the freeze-dried sources is 0.178 (1), slightly lower than 0.180 (3) for the nitrogen-dried sources. However, this part of the study was done with a limited number of sources (5 freeze-dried sources and 6 sources dried with the nitrogen-jet system), thus preventing a detailed statistical analysis of the experimental results; only a suggested trend can be observed.

4. Conclusion

The preparation of ^{51}Cr solid sources using the two drying techniques, freeze-drying and evaporation with hot-nitrogen jets, has been carried out for a comparative study. In order to characterize the influence of self-absorption as a function of the deposited mass, coincidence and photon spectrometry measurements were performed. The homogeneity of the radioactive sources was checked by autoradiography.

In the case of the photon spectrometry measurements, no significant difference between the two drying techniques was observed. It should be noted that the additional measurements of sources dried under atmospheric pressure gave significantly lower values. Moreover, the fact that no correlation arises depending on the deposited masses is particularly interesting. Because freeze-drying is time-consuming, the IRMM system seems to be better suited for the preparation of dry sources for photon spectrometry measurements.

By coincidence measurements, a large variability was observed. As expected, when a proportional counter was used, the results confirmed that the detection efficiencies for electrons are very sensitive to self-absorption and radioactive homogeneity defects. When comparing the two drying techniques, higher detection efficiencies have been obtained with freeze-dried sources (for masses above 12 mg). Nevertheless, we cannot draw definitive conclusions, because unexpected homogeneity defects were encountered on the sources dried with hot-nitrogen jets.

In this comparative study, encouraging results were obtained. However, they need to be confirmed or even improved with additional experiments. In the near future, an exercise is planned on ^{54}Mn solid sources in order to study the effect of an increase of carrier concentration.

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