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Use of WetSEM® capsules for convenient multimodal scanning electron microscopy, energy dispersive X-ray analysis, and micro Raman spectroscopy characterisation of technetium oxides

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Abstract

SEM–EDX and Raman spectroscopy analysis of radioactive compounds is often restricted to dedicated instrumentation, within radiological working areas, to manage the hazard and risk of contamination. Here, we demonstrate application of WetSEM® capsules for containment of technetium powder materials, enabling routine multimodal characterisation with general user instrumentation, outside of a controlled radiological working area. The electron transparent membrane of WetSEM® capsules enables SEM imaging of submicron non-conducting technetium powders and acquisition of Tc Lα X-ray emission, using a low cost desktop SEM–EDX system, as well as acquisition of good quality μ-Raman spectra using a 532 nm laser.

Keywords Electron microscopy · Raman spectrometry · Technetium oxides

Introduction

Technetium (Tc) is a high-yield fission product of both plutonium and uranium (6% fission yield for ^{235}U). In the safety case for geological disposal of radioactive wastes, ^{99}Tc makes a significant contribution to the long term dose risk, due its long half-life ($t_{1/2} = 2.1 \times 10^5$ years), and the high solubility and poor sorption of the pertechnetate species, TcO_4^- [1–3] In the context of some advanced nuclear fuel reprocessing flowsheets, such as the UREX process [4], an objective is to separate and immobilise Tc in a durable glass, ceramic or metal alloy wasteform for geological disposal[5, 6]. Consequently, there is considerable research directed at the synthesis and characterisation of Tc wasteforms and understanding the sorption and migration behaviour of Tc in engineered barrier systems relevant to their geological disposal [3, 7].

Tc is a soft (293 keV) beta emitter, with moderately high specific activity (6.2×10^8 Bq.g^{-1}) and thus must be handled in an appropriate radiochemical laboratory to prevent inhalation of particulates and transfer of contamination through volatilisation. This, combined with the need to isolate Tc from spent nuclear fuel in sufficient quantity for research purposes, means that the fundamental chemistry of this enigmatic element, with oxidation states spanning Tc -1 to $+7$, remains somewhat adolescent, despite the importance to nuclear fuel cycles [8]. For example, the synthesis and chemistry of the alkali metal pertechnetates were only definitively established in the last decade [9, 10].

Scanning electron microscopy (SEM), coupled with energy dispersive X-ray analysis (EDX), is an essential characterisation technique employed in materials science to examine the microstructure, morphology and elemental composition of materials with spatial resolution. Similarly, μ-Raman spectroscopy is a useful characterisation technique for the elucidation of material structure with spatial resolution. However, application of these techniques to characterise materials of moderately high specific activity, such as ^{99}Tc, typically demands use of dedicated instrumentation within a controlled area, to manage contamination. Moreover, examination of friable powder samples poses a further

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challenge due to the risk of inhalation. Consequently, we have considered how analysis of such specimens could be achieved with multi-user instruments, outside of a *controlled area*[1] whilst adequately managing the radiological risk [11]. Previous studies, such as Soderquist et al. have prepared Tc samples for SEM–EDX by depositing powdered material on a sticky carbon tab [12], although generally effective for powdered material, the possibility of Tc-bearing material becoming dislodged during measurement renders this method unsuitable for use outside of controlled areas or dedicated equipment for radioactive specimens. McKeown et al. used silica vials as a method of containment for Raman analysis of Tc-bearing glasses [13], however, this method of containment is unsuitable for SEM study and requires the preparation of an additional sample for both characterisation methods to be used.

Our attention was drawn to WetSEM® methods which have been successfully developed to allow the imaging of hydrated biological samples under atmospheric pressure whilst maintaining isolation from the vacuum of the SEM chamber [14, 15]. This method was also applied to the study of non-biological materials that are strongly affected by their degree of hydration e.g. shaving foam and silver nanoparticles [16, 17]. The method uses a disposable cold-seal capsule to isolate the hydrated substance, with a thin electron transparent window to allow imaging. We considered that such a capsule could also adequately function as a device for containment and multimodal SEM–EDX and μ-Raman analysis of radiological specimens, with moderately high specific activity, such as ^{99}Tc, without the need for dedicated instrumentation. Notably, Buck et al. recently reported in situ observation of uranyl oxide precipitation from solution, using the WetSEM® approach, however, the capsule was primarily intended to provide *liquid* rather than *radiological* containment [18]. Here, we demonstrate the use of WetSEM® capsules to contain and undertake spatially resolved SEM imaging, EDX analysis, and μ-Raman spectroscopy of ^{99}Tc bearing oxides, using a low-cost benchtop SEM–EDX instrument and Raman microscope, in a multi-user laboratory, outside of a *controlled area*. We show how we have used this method to support routine investigation of ^{99}Tc compounds in our laboratory.

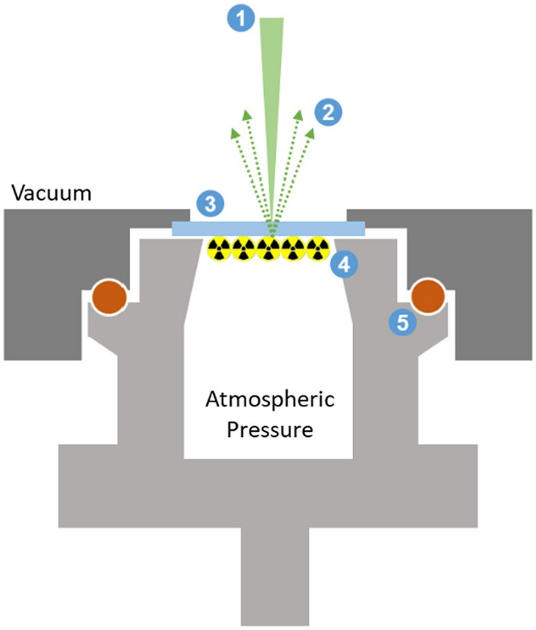

Fig. 1 Schematic diagram of WetSEM® capsule during observation. (1) Incident electron/laser beam, (2) Backscattered electrons/laser beam, (3) Membrane, (4) Radioactive material and (5) O-ring/seal

Materials and methods

Containment of ^{99}Tc specimens was achieved by the use of a Quantomix® QX102 WetSEM® capsule (El-Mul Technologies Ltd.), shown schematically in Fig. 1. During analysis, the incident beam (1) passes through the electron transparent membrane (polyimide, thickness 145 nm [19]) (3), interacts with the radioactive sample adhered to the membrane (4) and the backscattered electrons pass back through the membrane towards the detector. Throughout analysis, the atmosphere within the capsule is maintained by means of an O-ring seal that is formed between the upper and lower parts of the capsule and tightened by a bayonet fitting (5). Powders were prepared for analysis by suspension in isopropanol, a small aliquot of the suspension was withdrawn and dropped onto the inner surface of the electron transparent membrane using a pipette and the solvent allowed to evaporate (with the upper part of the capsule upturned). The capsule was sealed, swabbed, and monitored for contamination, before SEM observation. Specimens were imaged using a Hitachi TM3030 microscope with Bruker Quantax EDX using an accelerating

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[1] The term *controlled area* is used in the context of the definition in the UK Ionising Radiations Regulations 2017 (IRR17) Guidance. Part 4—Designated Areas [11]. A *controlled area* is "an area in which:

(a) it is necessary for any person who enters or works in the area to follow special procedures designed to restrict significant exposure to ionising radiation in that area or prevent or limit the probability and magnitude of radiation accidents or their effects; or.
(b) any person working in the area is likely to receive an effective dose greater than 6 mSv a year or an equivalent dose greater than 15 mSv a year for the lens of the eye or greater than 150 mSv a year for the skin or the extremities.".

In the UK, work requiring the use of weighable quantities of ^{99}Tc would typically be undertaken in a *controlled area* to manage the radiological risk.

voltage of 15 kV. The emission current was 1850 mA and beam current was 31.5 µA. µ-Raman spectroscopy was performed using a Horiba XploRA Plus spectrometer utilising a 532 nm laser, laser power was limited to 0.25 mW to avoid heating and potential damage of the membrane, the spot size was 20 µm.

For the purpose of method development, a capsule containing inactive MoO_2 and TiO_2 (Sigma-Aldrich, as received) was first prepared; the MoO_2 and TiO_2 powders were mixed, in a 1:10 mol ratio, by shaking in a glass vial. Inactive testing served three purposes: first, to perfect capsule loading, sealing, and decontamination methods; second to determine whether it would be possible to distinguish the materials by Z-contrast; and, third, to determine if it would be possible to detect the tender Mo Lα X-ray emission as a proxy for Tc Lα (Mo Lα1 = 2.2921 keV; Tc Lα1 = 2.4231 keV [20]). We strongly advise initial inactive testing to those following this methodology, in particular to perfect sealing of the capsule and decontamination procedure.

Caution. ^{99}Tc is a weak beta emitter ($E_{max} = 292$ keV). All manipulations were performed in a materials radiochemistry laboratory in a controlled area, using HEPA-filtered fume hoods and a dedicated negative pressure glove box, following risk assessments and monitoring procedures. WetSEM® capsules were prepared in the controlled area prior to transfer of specimens to the SEM–EDX instrument located outside of the controlled area.

After the methodology was successfully perfected with inactive materials, ^{99}Tc specimens were prepared. $Ti_{0.9}Tc_{0.1}O_2$ was synthesised by solid-state reaction between TiO_2 and TcO_2. Precursor powders were combined in the desired stoichiometric ratio, homogenised by grinding in a mortar and pestle using isopropanol as a carrier liquid and then heat treated at 900 °C for 8 h under flowing nitrogen in a tube furnace. $TlTcO_4$ was precipitated by adding a stoichiometric amount of $TlNO_3$ to an aqueous solution of NH_4TcO_4, the recovered material was filtered, washed and dried before analysis. $Ti_{0.9}Tc_{0.1}O_2$ and $TlTcO_4$ were confirmed to be single phase materials from analysis of X-ray diffraction data (XRD) and reference to the ICDD PDF 4 database, see Figure S1 and S2. XRD data were acquired using a Bruker D2 Phaser instrument, with Ni filtered Cu Kα radiation, in reflection mode, with a position sensitive detector. WetSEM® capsules are unsuitable as a means of containment for laboratory XRD measurement as a result of the minute quantity of sample and uncertainty in height displacement; containment of powder XRD samples was therefore achieved by using a sealed sample holder with a PMMA (polymethy methacrylate) dome.

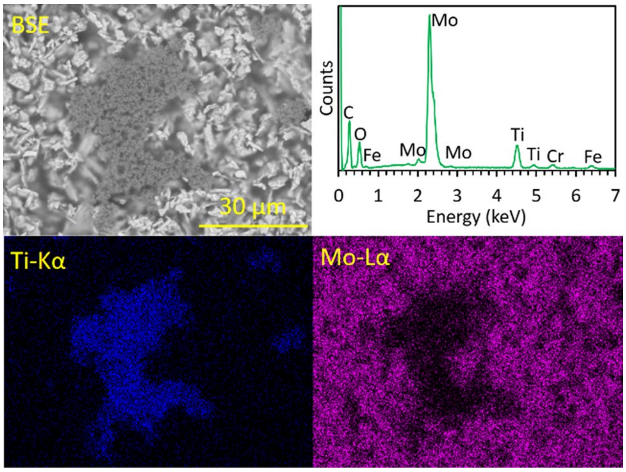

Fig. 2 Characterisation of mixture of MoO_2 and TiO_2 (1:10 mol ratio) by SEM–EDX using WetSEM® QX-102 sample containment, showing BSE image, EDX spectrum and EDX maps

Results and discussion

Figure 2 shows a Back-Scattered Electron (BSE) image, EDX spectrum and EDX map of the inactive mixture of TiO_2 and MoO_2, within a WetSEM® capsule. Clear BSE images were obtained through the capsule window, giving confidence that the window was sufficiently conductive to avoid charging of the powder sample, which did not have a conductive coating. It was possible to easily distinguish the different components of the specimen according to Z contrast, bright contrast corresponding to MoO_2 and dark contrast to TiO_2. The unique morphology of the component powder grains was also distinguished: MoO_2 particles were platelets a few µm in size, whereas TiO_2 particles were spherical and few 100 nm in size. Mo Lα and Ti Kα emission lines (2.2921 and 4.5122 keV) were clearly observed in the EDX spectrum acquired from the field of view in Fig. 2. The observed Fe Kα, Cr Kα and Ni Kα emission lines are a result of secondary electron interaction with the stainless steel grid used to support the electron transparent membrane, although this is not within the field of view. BSE observations were supported by EDX maps, in which Mo Lα and Ti Kα emission were clearly resolved but not co-located. This inactive development work provided confidence that the presence of a Tc compound present in a mixture of phases could be identified by Z contrast and EDX analysis.

Figure 3a shows a BSE image of $Ti_{0.9}Tc_{0.1}O_2$ with associated EDX spectrum and EDX maps, obtained using a WetSEM® capsule. The BSE image shows the presence of particles of uniform contrast and size, consistent with the presence of a single phase material; however, one small region of bright contrast was observable indicating the presence of a higher average Z or more conductive secondary

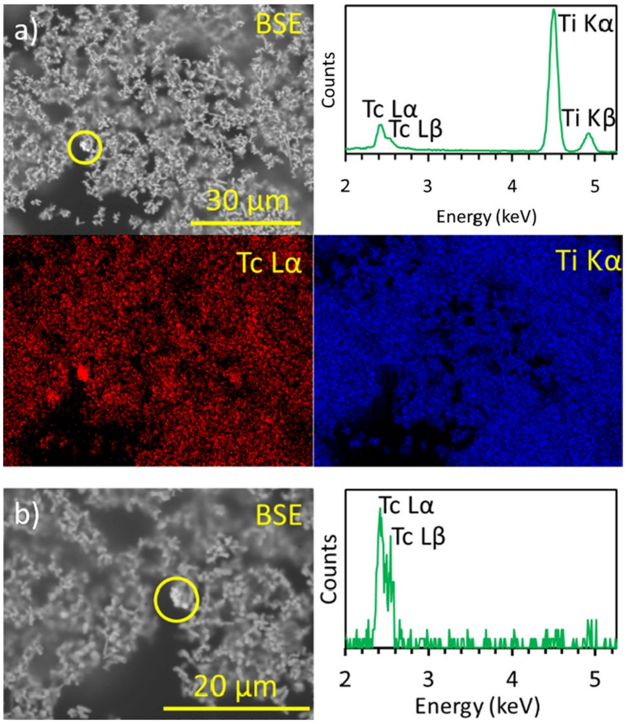

Fig. 3 Characterisation of $Ti_{0.9}Tc_{0.1}O_2$ by SEM–EDX using WetSEM® QX-102 sample containment a) BSE image, EDX spectrum and EDX map (acquired from full field of view), with region of Tc concentration highlighted by yellow circle and b) Higher magnification image and EDX spectrum acquired from within yellow circle, by post processing of data

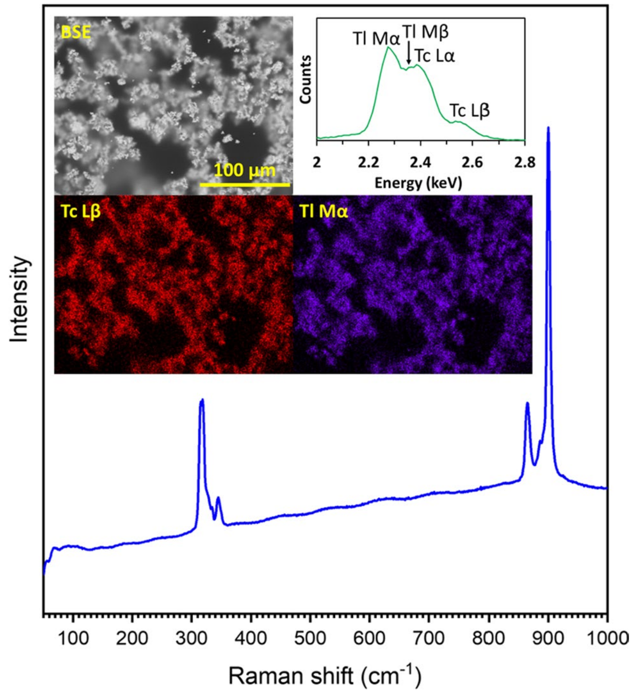

Fig. 4 Characterisation of $TlTcO_4$ by SEM–EDX using WetSEM® QX-102 sample containment showing a representative Raman spectrum of $TlTcO_4$, and, inset, sample imaged by SEM–EDX. EDX map constructed from Tl Mα and Tc Lβ emission, due to overlap of the former with Tc Lα

phase, albeit in low concentration. The imaged particle size is a few 100 nm, much smaller than the particle size of the reagents which was > 1 µm. EDX spectra and maps show Ti Kα and Tc Lα emission are clearly observed and co-located, consistent with the synthesis of a $Ti_{0.9}Tc_{0.1}O_2$ solid solution. It is also possible to identify a region of relatively high Tc concentration in association with the bright contrast observed in the BSE image; post-acquisition processing of EDX data, Fig. 3b, showed only Tc Lα and Lβ emission, thus demonstrating reduction to metallic Tc. As the EDX data were gathered by rastering the entire viewed area with the electron beam and there is no evidence of further reduced Tc, it is believed that the Tc metal observed is indeed a processing contaminant and not a result of interaction with the electron beam. As can be seen from Fig. 3, the coverage of the observable area was incomplete and, therefore, concentrated suspensions of the specimens are preferable to achieve complete coverage of the membrane in the focal plane (material located below the focal plane is evidently not imaged effectively but does not complicate the observation).

A further application of WetSEM® capsules is acquisition of both SEM–EDX and µ-Raman spectroscopy data from the same specimen, as far as we are aware this is this is the first such demonstration of acquisition of µ-Raman spectra from WetSEM® capsules. Figure 4 shows an SEM–EDX image of sub-micron grains of $TlTcO_4$, with a homogeneous distribution of Tl and Tc as determined from the EDX map constructed from Tl Mα and Tc Lβ emission, due to overlap of the former with Tc Lα emission. Analysis of the same specimen area using µ-Raman spectroscopy afforded a spectrum of good signal to noise ratio, albeit with relatively high background and some oscillating structure. Nevertheless, Raman bands were clearly evident and permit accurate determination of Raman shifts, see Table S1, which are comparable to those of other alkali pertechnetates [10, 21]. The most intense Raman band is associated with the symmetric stretch of the Tc-O bond of the TcO_4^- anion at 900 cm^{-1} (A_g mode), demonstrating potential for reliable Raman speciation of pertechnetate compounds using WetSEM® capsules.

The WetSEM® capsules in this study were employed as a means of containment for radiological powders. The containment afforded by these capsules offers the potential benefit of not dehydrating hydrated salts *in vacuo* as demonstrated by its use with pathology specimens [14, 15]. This is particularly attractive for the analysis of pertechnetate salts that are known to possess several hydrated forms and are sensitive to their degree of hydration [21–25]. Furthermore, the capsules are easily stored in a protective case enabling convenient repeat imaging if desired, the sealed unit preventing transfer of contamination. Indeed, we have successfully repeat imaged Tc specimens in WetSEM® capsules over 12 months. Gassman et al. used a modified membrane box with quartz windows as a means of sample containment [21], however, while effective for the simple alkali pertechnetates ($NaTcO_4$, $KTcO_4$), this was found to be insufficient for the more hygroscopic complex alkali technetium oxides investigated by Weaver et al. [25, 26]. Although effective containment has been demonstrated in this study for the pertechnetate salt $TlTcO_4$, it remains to be seen whether problems similar to those experienced by Weaver et al. would occur if studying highly hygroscopic materials.

This investigation utilised a desktop SEM–EDX system, with a W filament source, to demonstrate analysis of $Ti_{0.9}Tc_{0.1}O_2$ and $TlTcO_4$ powders using a multi-user instrument not dedicated to radiological material analysis, outside a controlled area. In our investigation, we did not observe any image distortion arising from charging of the non-conductive specimens, which were not coated with a conductive layer (e.g. carbon or gold). This is thought to be a consequence of both the use of low beam current achievable with a desktop SEM–EDX system and the conductive nature of the stainless steel membrane support which adequately dissipates charge.

Conclusions

WetSEM® capsules were found be effective containment for SEM imaging, EDX analysis, and µ-Raman spectroscopy of ^{99}Tc powder specimens with moderately high specific activity, using $Ti_{0.9}Tc_{0.1}O_2$ and $TlTcO_4$ as a demonstration. Specimens were analysed in a general purpose SEM–EDX system outside of a controlled radiological area with safe management of the hazard and risk of particulate contamination, afforded by capsule containment. The successful outcome of this proof of concept study was facilitated by development of capsule loading, sealing and decontamination using non-radioactive surrogate specimens, which is recommended. The information provided in this article is for general information purposes only and no responsibility or liability is or will be accepted by the authors in relation to it. Any use of the information or reproduction of the methods used are the responsibility of the user.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10967-021-07737-5.

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Declarations

Conflict of interest The authors declare no conflicts of interest relating to the publication of this work.

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