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Supporting information

# Quantification of technetium-99 in wastewater by means of automated on-line extraction chromatography – anion-exchange chromatography – inductively coupled plasma-mass spectrometry

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## 1. Comparison of studies using ICP-MS for the detection of $^{99}$Tc in aqueous samples with their LODs

**Table 1.** Compilation of studies using ICP-MS for the detection of $^{99}$Tc mostly in aqueous samples, complemented by their LODs and analyzed samples, in the order of the year each study was published. The lowest reported LOD from this selection is underlined.[1–5]

| Authors | Year | Sample | Vol. | Time | LOD |
|---|---|---|---|---|---|
| Momoshima *et al.*[1] | 1993 | Seawater | 1.4-3 $m^3$ | >7 d | 1.7 $fg·L^{-1}$ (1.1 $mBq·m^{-3}$) |
| Hill *et al.*[5] | 2000 | $^{99m}$Tc-gen. eluate | <10 mL | ~1 h | 50 $ng·L^{-1}$ (32 $Bq·L^{-1}$) |
| Skipperud *et al.*[4] | 2006 | Water/urine | <10 mL | ~1 h | 1 $ng·L^{-1}$ (6 $Bq·L^{-1}$) |
| Shi *et al.*[2] | 2012 | Seawater | 200 L | 12 h | 12 $fg·L^{-1}$ (7.5 $mBq·m^{-3}$) |
| Matsueda *et al.*[3] | 2021 | Reference | 50 mL | ~1 h | 9.3 $pg·L^{-1}$ (5.9 $mBq·L^{-1}$) |
| | | Seawater | 40 L | 10 h | 70 $fg·L^{-1}$ (44 $mBq·m^{-3}$) |
| Horstmann *et al.* *(this study)* | 2024 | Reference<br>Wastewater | 110.35 mL<br>1 L | 75 min<br><6 h | 6.3 $fg·kg^{-1}$ (4.1 $mBq·m^{-3}$)<br><u>0.70 $fg·kg^{-1}$ (0.45 $mBq·m^{-3}$)</u> |

## 2. Comparison of studies not using ICP-MS for the detection of $^{99}$Tc in aqueous samples with their LODs.

**Table 2.** Compilation of studies using radiometric techniques for the detection of $^{99}$Tc in aqueous samples, complemented by their LODs and analyzed samples, in the order of the year each study was published. The lowest reported LOD from this selection is underlined.

| Authors | Year | Sample type | Vol. | Time | LOD |
|---|---|---|---|---|---|
| Matsuoka et al.[6] | 1990 | Seawater | 300 L | >48 h | 77 fg·L-1 (49 mBq·m-3) |
| Harvey et al.[7] | 1991 | Seawater | 40 L | >12 h | 0.6 pg·L-1 (0.4 mBq·L-1) |
| Chen et al.[8] | 1994 | Seawater | 500 L | >32 h | <u>5 fg·L-1 (3 mBq·m-3)</u> |
| Barrera et al.[9] | 2016 | Seawater/urine | 10 mL | >24 h | 0.6 ng·L-1 (0.4 Bq·L-1) |
| Guérin et al.[10] | 2017 | Drinking water | 40 mL | >4 h | 8 ng·L-1 (5 Bq·L-1) |

## 3. Common parameters for all instruments used in the on-line ExC-IC-ICP-MS method

Common parameters for all instruments used in the on-line ExC-IC-ICP-MS method can be found in table 1. Parameters that were tuned daily with regards to the signal-to-noise ratio on the monitored $m/z$ of 99 and 101, are marked with an asterisk.

**Table 3.** Common analysis parameters for all instruments.

| Instrument | Parameter | Value |
|---|---|---|
| ICP-MS | RF Power | 1600 W |

| | | |
|---|---|---|
| *(Agilent 7700x, Pt cones)* | RF Matching | 1.59 V |
| | Sample Depth* | 5.7 mm |
| | First Extraction Lens* | -32.0 V |
| | Second Extraction Lens* | -200.0 V |
| | Omega Bias* | -104 V |
| | Omega Lens* | 6.1 V |
| | Cell Entrance* | -58 V |
| | Cell Exit* | -60 V |
| | Deflect* | 14.0 V |
| | Plate Bias* | -45 V |
| | Octopole Bias* | -8.5 V |
| | Octopole RF* | 200 V |
| | Energy Discrimination* | 7.1 V |
| | Monitored $m/z$ | 99<br>101 |
| | Dwell time | 0.4 s |
| | Analysis time | 200 s |
| Aerosol desolvation unit | Nebulizer Gas Flow (Ar) * | 0.85 L min$^{-1}$ |
| *(Apex 2)* | Makeup Gas Flow (Ar) * | 0.311 L min$^{-1}$ |
| | Add-Gas Flow ($N_2$) * | 3.9 mL min$^{-1}$ |
| | Spray Chamber Temp. | 140°C |
| | Condenser Temp. | 3°C |
| Cation suppressor | Regen. flow ($H_2SO_4$) | 2.3 mL min$^{-1}$ |
| *(Dionex ACRS 500)* | Regen. conc. ($H_2SO_4$) | 0.15 M |

## 4. Individual recovery data for ExC column and IC column

Both columns as well as the cation suppressor were tested individually for their recovery with diluted solutions of the in-house prepared and counter-quantified $^{99}$Tc standard, by comparing direct injections with their respective column injections. For the experiments a smaller loop size of only 50 µL was used to speed up the overall injection time. The recovery data are depicted in table 2.

**Table 4.** Recovery data for ExC column, IC column and cation suppressor.

| Method segment | c($^{99}$Tc) [ng L$^{-1}$] (50 µL injection) | c($^{99}$Tc) [pg L$^{-1}$] (assuming 110.35 mL load volume | Recovery in % |
|---|---|---|---|
| IC column | 10 | 4.53 | 94 ± 3 |
| | 50 | 22.7 | 97 ± 2 |

| | | | |
|---|---|---|---|
| | 100 | 45.3 | 102 ± 1 |
| | 500 | 227 | 103 ± 2 |
| | 1000 | 453 | 101 ± 1 |
| ExC column | 100 | 45.3 | 104 ± 2 |
| Suppressor | 100 | 45.3 | 94 ± 2 |

All components of the workflow show quantitative recovery. Determining the ExC column recovery proved difficult as peak widths between column and direct injection differed significantly between 12 s (direct injection) and >100 s (column injection), which might cause some slight overestimation of recovery due to more noise added to the peak. However, with the overall IBDA recovery being determined as quantitative, the individual recovery of the ExC column was considered equally quantitative.

## 5. Normalized chromatograms (*m/z* 99) from the recovery experiment of the ExC filter disk

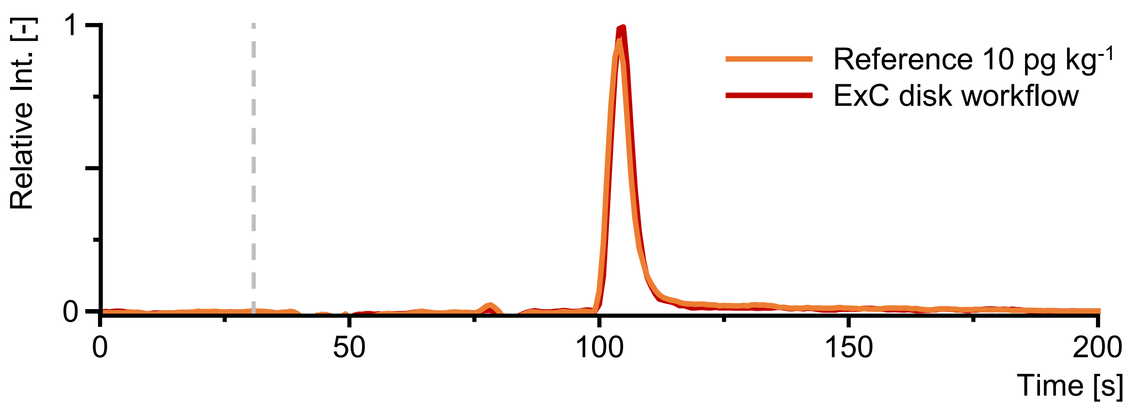


**Figure 1** Normalized chromatograms (*m/z* 99) from the recovery experiment of the filter disk, impregnated with the TK201 ExC extractant, indicating quantitative recovery of $[^{99}Tc]TcO_4^-$. The grey dashed line indicates the switching point between the two eluents at about 30 s.

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