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C-14/I-129 PRESERVATION AND HOLD TIME SURVEY

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Executive Summary

Preservation and hold time of radionuclides must account for both nuclear half-lives and non-nuclear loss mechanisms, but variations in the latter are often neglected. Metals-based defaults are inappropriate for long-lived non-metals C-14 and I-129, which are vulnerable to chemical and biological volatilization. Non-acidification is already widely practiced for them. Recommended addition measures from radiological and chemical literature include glass containers where possible, water filtration where possible, headspace minimization, light shielding, cold (4°C) storage and unfiltered water hold time of 28 days. Soil hold time may need to be shortened when water-logged, excessively sandy, or still adjusting to significant new contamination. Table 1 below summarizes recommendations.

Table 1: Summary of C-14/I-129 Preservation and Hold Time Guidance

Matrix	Collected Fraction	Preservation	Hold Time
Water	Total	Min. headspace, 4±2°C, amber glass or glass/PTFE stored dark	28 days
	Dissolved (0.22µ or 0.45µ filter)		180 days
Soil: watery, very sandy, or newly contaminated	Total	Min. headspace, 4±2°C, amber glass or glass/PTFE* stored dark	28 days
Soil: other/typical		Min. headspace, 4±2°C, glass/plastic*	180 days

* Normal soil self-shields for light, but small volumes may need control via container or dark storage.

Introduction

Almost all commonly-measured radionuclides are metals. EPA assigns metals preservation and hold time controls to gross alpha and beta, alpha-Radium and Ra-228. Those controls are acidification for water (pH < 2 with HNO3), nothing or refrigeration for soil (varies by EPA program), and hold time limits of 180 days for both. For example, EPA SW-846 (reference 1) chapter 3 table 3-2 agrees with 9000-Series radiological methods. EPA lacks modern methods for non-metals, but 70s-era drinking water methods (reference 2) for tritium and I-131 avoided acidification and emphasized I-131's very limited 8-day half life.

Physics-based practitioners have often extrapolated EPA's radiological guidance to additional nonmetal nuclides as a half-life-adjusted default without considering biological and chemical limitations. However, Carbon and Iodine in natural media are quite vulnerable to chemical and biological loss over much less than 180 days. Mitigating controls – sometimes even EPA limits – are published for the chemical species though not always the radiological versions. This paper surveys some of them. The radiological community needs a more consistent awareness of changes to default controls needed for C-14 and I-129 samples.

Methodology

Analyte names related to C-14 and I-129 must be identified for a proper literature survey. They need not be exact synonyms or analogs, but should broadly overlap the target nuclide. Table 2 lists such terms used for the literature comparisons to be discussed.

One potential source of confusion deserves special note. Results for C-14 and I-129 are typically reported on a total basis. Water samples can be filtered for later measurement and reporting of nuclides on a dissolved basis. Comparable chemical analytes in literature are sometimes termed "total" merely when non-speciated, so discussion of water sample handling must be carefully followed to ascertain filtration status.

Table 2: Comparable Analyte Names for C-14 and I-129

Radiological Analyte	**Comparable Chemical Analytes***
(Total) C-14, Radiocarbon	Total Carbon (TC), Total Inorganic Carbon (TIC), Total Organic Carbon (TOC), Oil & Grease (O&G) / Hexane Extractable Material (HEM), Petroleum Hydrocarbon Material, Natural Organic Matter (NOM), Extractable Organic Halides (EOX)+
(Total) I-129, Radioiodine^	Iodine, Volatile Iodine, Organic Iodine, Iodide, Iodate
Dissolved C-14, Dissolved Radiocarbon	Dissolved Carbon (DC), Dissolved Inorganic Carbon (DIC), Dissolved Organic Carbon (DOC), Total Organic Halides (TOX)+
Dissolved I-129, Dissolved Radioiodine	Dissolved Iodine, Dissolved Organic Iodine (DOI), Dissolved Iodide, Dissolved Iodate

^ Can refer to I-131 or both. * Overlaps to radiological, not always internally. + Also comparable to Iodine

Discussion

The literature demonstrates broad linkage of the environmental cycles for Carbon and Iodine. Organo-iodides are often the dominant environmental species of Iodine in water media (reference 3) as well as soil media (reference 4). Fehn, Snyder and Muramatsu (reference 5) even propose that "the strong association of iodine with organic material and the presence of … ^{129}I make the iodine isotopic system useful in tracing and dating organic materials." The petroleum industry already uses geologic anomalies of stable Iodine to locate hydrocarbon seeps (reference 6). Joint sample collection for C-14 and I-129 at remediation sites is thus well supported, and discussions below on vulnerabilities and controls will assume joint sampling.

Some direct guidance for C-14/I-129 sample controls is available from regulatory agencies. EPA's Inventory of Radiological Methodologies (reference7) text recommends: no acid, minimum headspace, cold (4°C), and consideration of glass versus plastic containers. (Options for additional chemicals can be shown to be unnecessary or counterproductive from further literature.) The USGS' TWRI water sample guidance (reference 8) covers only C-14, but calls for the same controls (mandatory glass) with the addition of dark storage. Indirect regulatory guidance via comparable chemical species like Iodide (reference 9) and TOC (references 1 and 9) limit holding to 28 days. International radiological practice generally follows these collection controls, although short holding is more typically emphasized in water studies (e.g., reference 10).

The primary challenge for Iodine and Carbon containerization is volatility. Initial volatile components need to be retained while further production needs to be inhibited. Any of the regulated volatile or semivolatile organic compounds, any unlisted one or the dissolved CO2 could carry C-14. Iodomethane or an unlisted volatile organo-iodide could carry I-129 and/or C-14. Elemental iodine sublimes, possibly carrying I-129, and often is in equilibrium with ionic forms. These possibilities argue for a tight seal with minimum headspace (gas phase) plus cooling (lower vapor pressure) per guidance. New volatilization of Carbon and Iodine can arise by means of oxidation (sometimes iodate reduction), photochemical reaction and microbial activity. Vulnerability to oxidation explains acid avoidance (explicit in reference 7) and further supports headspace (oxygen) minimization. Photoreactivity (e.g., organo-iodides in reference 11) explains light-shielding guidance. Microbial degradation further explains cooling (explicit in reference 7) and light shielding. More will be said about these volatilization mechanisms later.

Another consideration with some C-14/I-129 samples is interaction with container material. Organic solvents in samples can penetrate or pass through polymer bottles, carrying radiologic components with them. Similarly, Iodine species have long been known (reference 12) to bind to plastics other than fluoropolymers (PTFE, teflon®) as they do with environmental organic matter. These factors explain guidance recommendations for glass containers.

The significance of microbial activity to Carbon and Iodine volatilization from water has been established by numerous studies. Köhler et al. (reference 13) reported 33-50% losses of NOM over 12 days from stream and soil water by combined light and microbial activity in an incubation experiment, although light was suggested as more important. Campos et al. (reference 14) reported idodate reduction to less stable iodide in surface waters by biological processes at about 100 times the rate of iodide incorporation into particulate organic carbon, with Iodide showing a resident half-life of 70 days. Amachi et al. (reference 15) reported biologic conversion of such iodide to volatile organic iodine, which could be halted by various forms of microbial inhibition.

Simple filtration has been found by a number of studies to be a highly effective interrupter of microbial activity. Reference 14 stated iodine "volatilization did not occur" after 0.22µ filtration. Buraglio (reference 16) used 0.45µ filtration and found stream I-129 values within 10% after up to 15 months of cold, dark storage. Tagami and Uchida (reference 17) found Iodine levels in filtered river water samples stored at 5°C did not change for almost a year. Doctor et.al. (reference 18) found that 0.2 µ filtration of stream DIC samples was as effective as common preservatives (poisons) in guarding against fractionation by biological activity over a 9 month period of cold, dark storage.

Soils generally accumulate Iodine, though they do off-gas (CH_3I) and can be leeched, all with important microbiological contributions. Whitehead (reference 19) found that soil organic matter binds iodine more effectively than mineral ion-exchangers like clay, while a sandy soil can volatilize half to all its iodine in 30 days. Sheppard et al. (reference 20) reported a dynamic partitioning of Iodine between soil organics and DOC under flooded conditions. Muramatsu and Amachi teams (references 21-23) concluded that "accumulation of iodine in soils was explained by the effects of microorganisms," including CH_3I-producing, Iodide-oxidizing and Iodate-reducing strains.

Antimicrobial measures inhibit both Iodine sorption and any volatilization (references 22-23). Since natural freezing is effective (reference 24), the artificial version applied to Volatile Organic Carbon (VOC) samples in recent years (reference 1 method 5035) might be worth considering for C-14/I-129 in extreme cases. However, traditional cooling (4°C) goes a long way with much simpler logistics. In practice, most soil samples for iodine are stable for most of a year to several years (reference 25).

Conclusion

Iodine and Carbon are linked in the environment and share vulnerabilities to loss from samples, supporting the practice of joint sampling for C-14 and I-129. Volatility is the main preservation concern, although penetration of polymer containers can occur. Acid addition would create artificial losses via rapid oxidation and must be avoided. Natural degradation with volatilization continues in samples via photochemistry and microbial action, unless they are inhibited. Preservation controls from existing guidance for C-14/I-129 and comparable chemical analytes include: glass containers where possible, water filtration where possible, minimum headspace, light shielding and cold storage.

Hold times for properly preserved C-14/I-129 samples are not directly regulated, so extensions of the 28-day chemistry times may be freely taken when warranted. Literature documents *filtered* water samples (dissolved constituents) lasting comfortably beyond the 180 days applicable to metals and their radionuclides. Stability in soils is generally much greater than in water, except when waterlogged, very sandy or still adjusting to significant new contamination, and literature supports a general 180-day limit. Unfiltered water and those extreme soil situations would be safer with the 28-day chemistry limit.

Recommendations are summarized in Table 1 of the executive summary.

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