



Taking part of the lab to the sample: *On-site* electrodeposition of Pb followed by measurement in a lab using electrothermal, near-torch vaporization sample introduction and inductively coupled plasma-atomic emission spectrometry

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ABSTRACT

An electrodeposition method for preconcentration and separation of labile Pb from liquid samples with a complex matrix is described. For the first time, Pb was electrodeposited *on-site* on Re coiled-filament assemblies that were developed for use with an electrothermal, near-torch vaporization (NTV) sample introduction system and inductively coupled plasma-atomic emission spectrometry (ICP-AES). The coiled-filament assemblies (or simply coils) were purposely designed to be removable and were fabricated to have identical coupling-mechanisms so that they can be used interchangeably. In addition to their small size (2.75 cm long and 0.65 cm wide), coiled-filament assemblies weighed only 1.4 g, which made them portable for *on-site* use. The detection limit from diluted seawater Certified Reference Material (CRM) and NTV-ICP-AES was 25 pg/mL following a 3 min electrodeposition. This detection limit represents a 40-fold improvement as compared to the detection limit obtained by pipetting 5 μ L of dilute Pb standard solution directly on the coil. The detection limit improved by 400-times (to 2 pg/mL) when the electrodeposition time was increased to 60 min. Lead from very hard tap water was electrodeposited on coiled filaments *on-site* using a shirt-pocket size, battery-operated potentiostat and portable electrodeposition instrumentation. Concentration was determined in the lab using NTV-ICP-AES. The Pb concentration was used to test for compliance with the Pb–Cu rule set by the United States Environmental Protection Agency (US EPA). Overall, *on-site* electrodeposition permitted determination of Pb at the environmental conditions (e.g., pH, temperature) recorded at the time of sampling. *On-site* electrodeposition also opens the possibility for shipping portable coils with Pb electrodeposited on them to the lab rather than shipping large volumes of sample, thus reducing shipping, handling and storage costs.

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1. Introduction

Recently, we described use of removable Re-coil filament-assemblies as sample holders for an electrothermal, near-torch vaporization (NTV)-inductively coupled plasma-atomic emission spectrometry (ICP-AES) system [1]. In NTV, a removable coiled-filament assembly with a sample pipetted on it is inserted into a small-size vaporization chamber that clips onto an ICP torch. The sample is dried by applying low electrical power to the coil. Subsequently, higher electrical power is applied to the coil thus vaporizing the remaining dried sample residue on it. The vaporized sample inside the chamber is transported to an ICP by a tangentially introduced carrier gas.

Rhenium coiled-filament assemblies were purposely fabricated to be removable and to have the same dimensions so that they can be used interchangeably. They were also intentionally designed to be small-size (e.g., less than 3 cm by 1 cm) and light-weight (e.g., 1.4 g), and thus portable. Interchangeable and portable coiled-filament assemblies

(or coils for short) were made from coiled Re filaments with volume-capacities ranging from less-than 100 nL to 100 μ L [1]. In particular, use of 100 μ L volumes of samples improved detection limits expressed in concentration units [1]. The improved detection limits enabled determination of Pb at the few 100s of pg/mL level by Re-coil NTV-ICP-AES in a sample with a relatively clean matrix, such as diluted natural water CRM (Certified Reference Material) [1]. Lead was chosen due to its environmental significance. The goal of this work was to investigate whether Re-coil NTV-ICP-AES can also be used for pg/mL determination of Pb concentrations from liquid samples with a complex matrix.

There are three inter-related objectives for this work. The first objective is to find out if interchangeable Re-coils can be used for determination of Pb at low pg/mL concentration-levels by NTV-ICP-AES from a sample with a challenging and complex matrix. In general, seawater is considered as a challenging liquid matrix by ICP spectrometry [2,3] due to its high salt content (~35 g/L or ~0.6 M assuming that all salt in seawater is NaCl). Furthermore, determination of Pb at low concentrations is regarded as one of the most challenging tasks due to the relatively poor detection limit for this element by ICP-AES [2]. For example, Pb determination at the pg/mL level is at or below the detection limit

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of commercial ICP-AES systems with pneumatic nebulization sample introduction.

To meet the first objective, a seawater CRM was used as a representative sample-type. Matrix clean up however is essential for such sample type, because the high salt content of seawater can cause spectral interference, stray light and matrix effects in ICP-AES [2]. In addition to interference, the high salt content can also block the sampler cones used with various types of ICP-MS [3] systems. Unlike the diluted natural water CRM mentioned earlier, the high salt content of seawater makes it impossible to use 100 μL volumes [1]. There will simply be too much salt left on the coil after drying. Thus, both preconcentration and matrix clean-up become necessary.

Methods of preconcentration and cleanup of seawater (and of other types of samples with complex matrices) are required not only for ICPs but for other atomic spectrometry methods as well (e.g., flames [4] and atomic absorption [5]). Examples of methods of preconcentration and clean up include solid phase extraction [6,7], cloud point extraction [8], liquid-liquid extraction [9] and methods utilizing nanomaterials [10–12]. All of these methods to some extent require sample-preparation, sample-manipulation and addition of reagents. Can preconcentration and clean up take place directly on interchangeable coiled-filament assemblies thus minimizing sample-preparation, sample-manipulation and reagent-addition and also provide concentration information at the environmental conditions (e.g., pH, temperature) that existed at the time of sampling?

Electrodeposition is a reagent-free matrix-separation and preconcentration method [13–15]. As such, it offers an attractive alternative to the methods mentioned above. In its simplest form, an electrodeposition setup consists of three parts: two electrodes; a solution containing metal ions of interest; and a power supply. The coiled-filament of an interchangeable assembly can be used as one of the electrodes. Furthermore, electrodeposition instrumentation can be made small-size and light-weight. In addition, a hand-held power supply that can be operated from a battery can be developed easily. These enable portability for use *on-site*.

Electrodeposition preconcentration and clean-up on graphite supports [16–26] and on metallic probes (including wires) [27–32] have been applied to a variety of samples with a difficult matrix (i.e., those with a high salt content, including seawater). Electrodeposition has been used primarily with atomic absorption spectrometry (AAS) including flame AAS [28,34], flameless AAS [27], electrothermal AAS [19–22,30–32], and to a lesser extent by ICP-AES [16–18] and arc emission spectrometry [26]. To our knowledge, electrodeposition has not been done *on-site* or on portable and interchangeable probes made from Re.

Provided that electrochemical Pb preconcentration and matrix clean up from seawater are possible on Re-coils, the second objective became to find out if there is analyte loss when Pb electrodeposited on a coil in one location (e.g., *on-site* and away from a lab) is transferred to another location (e.g., to a lab) for concentration-determination NTV-ICP-AES.

If there was no analyte loss during transport, the third objective became to demonstrate transferability of the Pb electrodeposition method developed for seawater in a lab to other sample types with a relatively complex matrix (e.g., very hard water [35]) and to show applicability for use *on-site*.

It will be shown that matrix clean up and Pb preconcentration on coiled-filaments are possible, that there is no loss of Pb preconcentrated on Re-coils (for the concentration levels tested) and that the method developed in a lab for seawater can be applied to another sample with a difficult matrix (such as hard groundwater) for use *on-site*. Analytical capability, utility and applicability of the *on-site* method will be demonstrated using tap water from an off-campus location to test for compliance with the United States Environmental Protection Agency (US EPA) Pb–Cu rule that stipulates that “if Pb concentration exceeds an action level of 15 ppb or if the Cu concentration exceeds an action level of 1.3 ppm in

more than 10% of the customers taps sampled”, corrective action must be taken.

2. Experimental methods

2.1. Instrumentation

A schematic illustration of the electrothermal, near-torch vaporization (NTV) sample introduction system for ICP-AES is shown in Fig. S1a (supplement). Using coupling optics [36], optical emission from the ICP was guided into the entrance slit of a direct reading spectrometer with photomultiplier tube (PMT) detectors. The output current from the PMT was amplified, digitized and stored on a computer. Only the Pb II 220.353 nm spectral line was used. Operating conditions are listed in Table 1. A schematic of a small-size, light-weight, portable and interchangeable coiled-filament assembly is shown in Fig. S1b. A photograph of the vaporization chamber with a removable coiled-filament assembly in it is shown in Fig. S1c.

Briefly, a removable coil-filament assembly (Fig. S1b) consists of a 9.5 mm-long, 6.5 mm diameter two-hole ceramic collar [1]. On one side of the ceramic, a coil-filament made from 250 μm Re-wire is installed. On the other side, two pins are installed inside the holes of the ceramic collar. The pins are connected to the coiled-filament through the linear part (or legs) of the coil. The pins are designed to fit effortlessly but tightly into mating sockets installed on a two-hole ceramic support rod (Fig. S1a). Assemblies were purposely fabricated to have the same dimensions, thus in addition to being removable they were also made interchangeable. Removable assemblies could be interchanged in about 10 s. The total length of a coiled-filament assembly was 2.75 cm and its maximum diameter was 0.65 cm. Such dimensions made interchangeable coil-filament assemblies small and their total weight of 1.4 g made them lightweight. Thus, their small-size and low-weight made them portable.

The ceramic support rod with an interchangeable assembly on it was manually inserted into the vaporization chamber (Fig. S1c) and it was stopped at its optimum insertion position [1]. A seal was formed

Table 1
Operating conditions.

<i>ICP:</i>	
Forward power	1000 W
Reflected power	<3 W
Outer tube gas	15 L/min
Intermediate tube gas	0.6 L/min
<i>NTV:</i>	
Carrier-gas composition	Ar–H ₂ (3%)
Carrier gas flow rate	0.7 L/min
Coil insertion position	22 mm
Drying power	~1 W
Drying duration	1.5 min
Vaporization power	25 W
<i>Multichannel spectrometer:</i>	
PMT power supply	–1000 V
Pb spectral line	220.353 nm
<i>Readout electronics:</i>	
Sensitivity	200 (nA/V)
Filter frequency	10 Hz
Filter type	Low-pass, –12 dB/octave
Data acquisition rate	100 Hz
Acquisition duration	10 s
<i>Electrodeposition:</i>	
Solution volume	20 mL
Applied cell potential	2.0 V
Deposition duration	3.0 min

Maximum operating temperature of the Re coil is >3000 °C [1].

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