



# Dynamic leaching and fractionation of trace elements from environmental solids exploiting a novel circulating-flow platform



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## ABSTRACT

A dynamic flow-through microcolumn extraction system based on extractant re-circulation is herein proposed as a novel analytical approach for simplification of bioaccessibility tests of trace elements in sediments. On-line metal leaching is undertaken in the format of all injection (AI) analysis, which is a sequel of flow injection analysis, but involving extraction under steady-state conditions. The minimum circulation times and flow rates required to determine the maximum bioaccessible pools of target metals (viz., Cu, Zn, Cd, and Pb) from lake and river sediment samples were estimated using Tessier's sequential extraction scheme and an acid single extraction test. The on-line AIA method was successfully validated by mass balance studies of CRM and real sediment samples. Tessier's test in on-line AI format demonstrated to be carried out by one third of extraction time (6 h against more than 17 h by the conventional method), with better analytical precision (< 9.2% against > 15% by the conventional method) and significant decrease in blank readouts as compared with the manual batch counterpart.

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## 1. Introduction

Elevated concentrations of metals in soils, sediments and airborne particulate matter might pose severe concerns to the public health. For example, the bioaccessible metal pools in sediments are known to influence the distribution and composition of benthic assemblages [1].

Risk assessment of trace element contamination in solid samples such as soils, solid wastes and river/ocean sediments is commonly undertaken by eluting the metals via leaching tests by utilizing water, electrolytes, acids (acetic acid or hydrochloric acid), reductants and oxidants as extractants so as to release target species associated to given mineralogical phases. Specifically, the purpose of leaching tests is to determine the aqueous phase concentrations of metals that are released from solids under environmentally simulated conditions, that is, the bioaccessible metal pools in environmental scenarios or alternatively when placed in land disposal units. The idea behind is to evaluate the potential harmful effects to biota and humans as a result of

leaching of metal species into groundwater through a soil body or into marine ecosystems. Numerous laboratory leaching or bioaccessibility tests have been reported over the past few decades [2–5]. For example, in the US and Canada, the toxicity characteristic leaching procedure (TCLP) [6] is a commonly utilized leaching test that employs acetic acid or acetic acid/acetate buffer (pH 2.88 or 4.93, respectively) to evaluate metal leaching from solid wastes. Also, leaching tests that utilize HCl, with or without pepsin, mimicking gastric digestion, assess potential hazardous effects to human health when bringing toxic metals from the mouth to the stomach by directly taking solids such as soil, sediment, fly ash, or toys [6–10].

Single extraction methods are used to provide a rapid snapshot of metal leaching from environmental solids or solid wastes [11,12]. However, sequential extraction or fractionation tests have been commonly the method of choice so as to provide regarding detailed insight into different metal–soil associations [2,4,5,13–17], by exploiting a number of extractants of increasing elution strength. Fractionation studies are aimed at determining the chemical forms in which metals occur, because metal mobility, bioaccessibility and bioavailability strongly depend on their chemical and mineralogical forms [2,4,5,13–17]. Sequential extraction protocols individually separate 4~6 pools of chemical forms of metal species that have different leachability, including the water soluble fraction, the ion-exchangeable fraction, the carbonate

*Abbreviations:* AI, all injection; AIA, all injection analysis; CRM, certified reference material; FAAS, flame atomic absorption spectrometry; RSD, relative standard deviation

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fraction, and metals bound to Fe–Mn oxyhydroxides and organic matter. The most widely accepted fractionation tests are the so-called 3-step BCR developed under the auspices of the Community Bureau of Reference (formerly BCR, but currently termed the Standard, Measurement and Testing (SM&T) Program of the Commission of the European Communities) [18,19], and the Tessier scheme [20], where bioaccessible metals are associated to the exchangeable, acid-soluble, reducible and oxidizable phases in soils and sediments. The classifications of chemical forms of metal species by sequential extractions are usually performed by batchwise methods with tedious and time-consuming unit operations such as filtration, centrifugation, and reagent replacement. Those manual operations are likely prone to sample contamination, and they often lead to poor data accuracy.

To overcome the above issues of batchwise bioaccessibility tests, novel (semi)automatic or fully automatic flow systems for dynamic extraction procedures that may afford the addition of extractant(s), on-line extraction of metals, filtration of remaining solids, and alternatively, on-line analysis of extracts have been developed over the past few years [21–34].

A common procedure for on-line dynamic bioaccessibility tests of metal species in environmental solids is as follows [26]: (1) a soil sample is packed into a reactor, e.g., coil, column, or chamber; (2) an extractant is brought into the reactor using a pump; (3) the leachates are analyzed off- or on-line by an atomic spectrometric detector. A flow-based setup configurations for fractionation schemes have been developed so that the extractants of each specific chemical form of target metals could be intermittently loaded into the reactor from reagent reservoirs by switching valves [31–34]. Miró et al. developed sequential extraction methods in a dynamic flow-through format based on the distinct generations of flow injection analysis so as to ameliorate the extraction efficiency and assure leaching of bioaccessible pools of trace metals under “worst-case” extraction conditions [25–27,30–34]. In the development of flow-based dynamic extraction systems, a great deal of attention has been focused on assembling analytical devices for repeatable unit operations and maximization of the reaction time between sample and reagent to get insight into the overall bioaccessible metal species.

In this study, a novel extraction system is proposed that could efficiently extract trace elements from riverbed sediment samples using a microcolumn and by circulating the extract instead of shaking, stirring or continuous pumping of the extractant (s) toward and through the packed column. This idea is based on the principle of all injection analysis (AIA), which was first described by Itabashi et al. [35]. In AIA, all solutions are injected into a reaction coil and are circulated for a pre-set amount of time at a fixed flow rate. Because the solution (extractant) feed is stopped during the circulation process, the reagent consumption is significantly decreased as compared with conventional continuous-flow or flow injection manifolds.

Our goal is to demonstrate whether a circulating-flow platform based on the AIA principle is a suitable flow-based method to obtain reproducible patterns of leached metal species. The extraction performance of the AIA device was evaluated using an acidic single extraction test and Tessier's sequential extraction procedure with the AIA features as a novel leaching approach critically compared against those of conventional batch leaching tests. As a practical application, sediments sampled along the Watarase River until Kusaki dam-lake located at the down-stream were on-line fractionated by the Tessier scheme in AIA fashion. As a result of mining activities from the Ashio copper area in Tochigi and Gunma Prefectures (1890s–1990s), large amounts of metal species were discharged to the Watarase river, whereupon appropriate sediment and water management schemes has been continuously performed.

## 2. Experimental

### 2.1. All injection-type device for metal leaching

The AI-type extraction device, AIA-IT3, was manufactured by Ogawa, Co., Ltd. (Kobe, Japan) and Kurahashi Giken, Ltd. (Kyoto, Japan) in cooperation with our research group. AIA-IT3 consisted of an 8-port rotary valve, a 4-port switching valve, a peristaltic pump, and a process control monitor (see details in Fig. 1). The tubes used to connect valves, sample-packed column, and reagent reservoirs were made of Teflon<sup>®</sup> (1 mm i.d.), and that of the pump was made of silicon (2 mm i.d.). The 4-port valve, which feeds the extractant into the re-circulation channel, was connected in series with the 8-port valve. The 8-port valve, in which the extractant leaches metals from the solid sample, as illustrated in Figs. 1 and 2. The sediment samples were packed into a microcolumn consisting of a Rezorian<sup>™</sup> cartridge (1 cm<sup>3</sup> of inner volume, 5 cm long, Sigma-Aldrich, St. Louis, MO, US). The samples (0.25 g) were loosely packed to a thickness of 10 mm in the column, and PTFE membrane filters (pore size: 0.20 μm; thickness: 20 mm, Advantec) were placed at both ends. The column was connected to the manifold via luer-lock adaptors and nuts (see magnified view in Fig. 1).

The sample-laden column was integrated in one of the loops of the 8-port rotary valve. The extractant was first loaded into the loop of the rotary valve (Fig. 2), and then circulated for a specific timeframe at a constant flow rate through the column.

### 2.2. Extraction procedure

The AI-based leaching procedure for leaching of trace elements from solids is schematically presented in Fig. 2. First, a given extractant is brought to the circulation channel at the 8-port valve (Fig. 2a), by activation of the peristaltic pump and selection of the appropriate port at the switching valve. By changing the valve position of the 8-port valve, the flow-line manifold is switched to a closed-line arrangement in order to circulate the extractant for a specific period, usually 0.5–5 h (Fig. 2b). During the extraction, the flow-line, except for the circulation channel, is stopped. Upon returning the valve to the original position, the re-circulated extract solution is flushed out from the 8-port valve with a pure water feed (Fig. 2c).

In our system, the circulation channel of the 8-port valve was filled with 1.5 or 2 mL solution, which was finally flushed out from the rotary valve and collected in a 20 mL volumetric flask. The volume was made up to 20 mL by adding pure water prior to analysis by flame atomic absorption spectrometry (FAAS, ca. 5 mL-per-injection). The detection instrument was a polarized Zeeman FAAS (Hitachi Z-5310, Japan). Hollow cathode lamps for FAAS were

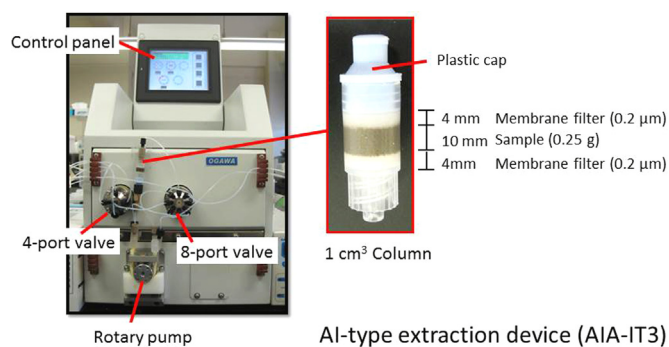


Fig. 1. Close-up of the AI-type extraction device (AI device) furnished with a sample-packed column for leaching tests of metal species in sediments. The inset illustrates a magnified view of the sediment containing microcolumn.

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