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Method study for the preparation of a wet sediment quality control material

A. Guevara-Riba [a], R. Rubio [a], G. Rauret [a], H. Muntau [b], A. Sahuquillo [a,*]

[a] *Departament de Química Analítica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*
[b] *University of Sassari, Via Vienna 2, 07100 Sassari, Italy*

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Abstract

Quality control materials (QCMs) to be used in daily quality control in environmental laboratories are required to be similar to real samples in terms both of composition and of physical state. The present paper describes in detail the procedure of preparation and the results of homogeneity and stability studies performed on wet sediments QCMs. For this purpose, two sediments with different matrix composition were selected and the main factors involved in the preparation of the material were carefully studied and established with the aim of guaranteeing long-term stability of the QCM: pre-treatment steps, homogenisation, bottling and storage. The results obtained from the homogeneity and from 12 months of stability studies for Cd, Cr, Cu, Ni, Pb and Zn following the *aqua regia* extraction procedure (ISO 11466), showed that the wet sediment QCMs we have developed are feasible, constituting a new and useful material among the aquatic sediments for quality control purposes in monitoring.

Keywords: Quality control material; Reference materials; Wet sediment; Trace metals analysis; Homogeneity studies; Stability studies

1. Introduction

Sediments are the part of the hydrological cycle which, depending on their chemical composition and adsorbing characteristics, may have the highest accumulation capacity for both inorganic and organic contaminants [1]. Moreover, changes in environmental conditions can easily lead to the re-release of contaminants into the aquatic system. This role of sediments as both a sink and a source of contaminants, has been a topic of research on environmental monitoring since years [2,3].

Most environmental studies described in the literature are performed on sediment samples dried once in the laboratory. However, the drying step can affect the kinetics of the extraction of trace metals and thus, the information on bioavailability [4,5]. It can also alter the extraction yield of certain organic compounds [6] and toxicity results from different bioassays [7,8]. The information obtained from dried samples may thus be different from that given by the direct handling of wet samples.

As the environmental management of water systems must be based on reliable analytical measurements, the use of certified reference materials (CRMs) for validation purposes, and quality control materials (QCMs) in interlaboratory exercises and in drafting control charts for checking long-term reproducibility, are advisable practices for laboratories [9]. Although both categories of materials must fulfill homogeneity and stability requirements, the effort dedicated to establish the final characterisation values of the established parameters can be much lesser for QCMs. The increasing demands on reference materials (RMs), including certified and non-certified materials, are focused on closer matrix-matching to environmental samples, not only regarding composition, analytes concentration, and possible interferences, but also regarding the physical state of the material [10–12]. Thus, the availability of a new class of aquatic sediments RMs with similar physical state as real environmental samples (wet RMs) would represent a valuable novelty for environmental quality control.

In the present work, and as a first attempt, we present a method study for the preparation of a wet sediment QCM. The study deals with sample pre-treatment and handling, especially during homogenisation and bottling. The established protocol was applied to two sediments with different matrix composition.

As it has been stated [13], the quality of an RM is supported by its homogeneity and stability. Furthermore, and as most directives [14,15] on environmental management include heavy metals as priority pollutants to be monitored, homogeneity and stability of the new material have been assessed focusing

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[*] Corresponding author. Tel.: +34 93 4021281; fax: +34 93 4021233.
E-mail address: angels.sahuquillo@ub.edu (A. Sahuquillo).

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this first study in the determination of Cd, Cr, Cu, Ni, Pb and Zn extractable contents in the wet sediment following an *aqua regia* extraction procedure according to ISO Standard 11466 [16].

2. Experimental

2.1. Location of the samples

The samples used in this work were provided by the Environmental Institute at the Joint Research Centre in Ispra, Italy [17,18]. Sampling was run by means of a Ponar grab which allowed taking out the first 10–15 cm depth in an area of around 40–50 cm^2 of sediment.

Fig. 1 illustrates the sampling site locations for deltaic sediment (River Po) and for the sediment from Venice (Rio Marine) chosen for this study.

2.2. Sample handling and preparation of the wet quality control sediments

After sampling, the sediments were wet sieved in situ to 2 mm with a stainless-steal sieve (Prüfsieb, Germany), to eliminate extraneous wastes (i.e. small brick pieces, glasses, different plastic residues, etc.), and they were immediately stored in polyethylene containers with seawater. Once in the laboratory, the first purpose was focused on reducing the natural water content with the aim of guaranteeing the long-term stability of the material. For this, the bulk material was mechanically stirred in a polyethylene container under a current of argon or nitrogen. The initial water content in the collected sediments measured in the laboratory (by drying the sediment at 100 ± 5 °C) was 71.8 and 64.5% in Po River and Venice sites, respectively. This water content was not significantly reduced after more than 10 h for both gases. Thus, the bulk material was left to settle overnight and a part of the supernatant water was removed with a syringe, reducing then the water content by an additional 10%. Samples were then stored at −18 °C until further handling.

For the preparation of the QCMs, sediments were first taken to room temperature and then stirred for homogenisation with a wooden bar. Then, the sediments were wet sieved at 250 μm in order to select the most appropriate fraction for heavy metals analysis (90–95% yield). The fraction under 250 μm (about 5 kg in the present work) was homogenised in a Pyrex container, using an Ultra Turrax® (IKA®, USA) stirrer and working at 10 000 rpm. A mechanical stirring with a stainless-steel helix was proved not to be efficient enough for homogenisation at this step. When using such a device it could be observed a supernatant water layer, risking an inhomogeneous distribution of water content during bottling. Thus, and even if the temperature of the Pyrex container with the bulk material was slightly increased after some hours of shaking, the Ultra Turrax device is recommended. For the bottling process, 10% HNO_3 precleaned glass weighing containers (dimensions: 2 cm diameter and 1.5 cm height, that is approximately 5 cm^3 capacity) were needed. These containers were identified with a number and

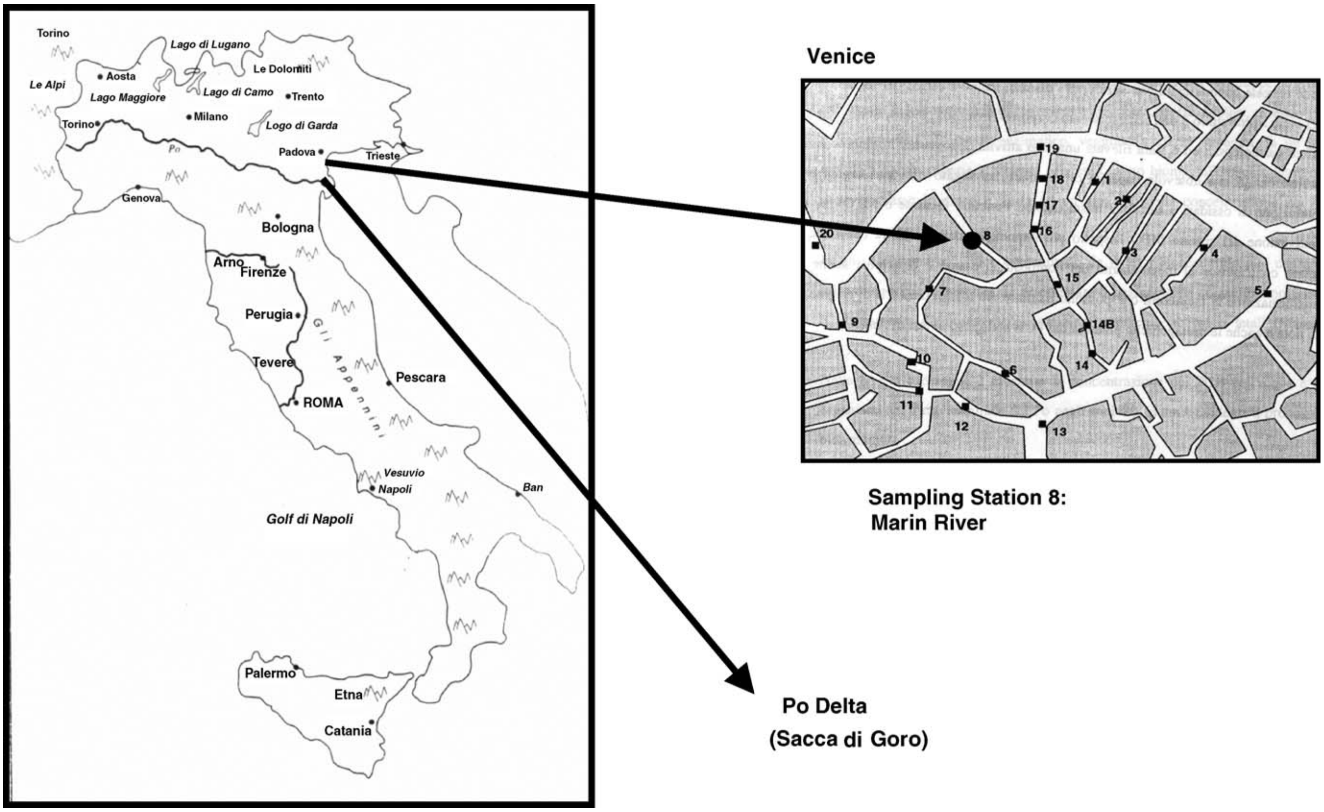

Fig. 1. Sampling sites for the collection of wet sediment materials.