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A community-wide intercomparison exercise for the determination of dissolved iron in seawater

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Abstract

The first large-scale international intercomparison of analytical methods for the determination of dissolved iron in seawater was carried out between October 2000 and December 2002. The exercise was conducted as a rigorously "blind" comparison of 7 analytical techniques by 24 international laboratories. The comparison was based on a large volume (700 L), filtered surface seawater sample collected from the South Atlantic Ocean (the "IRONAGES" sample), which was acidified, mixed and bottled at sea. Two 1-L sample bottles were sent to each participant. Integrity and blindness were achieved by having the experiment designed and carried out by a small team, and overseen by an independent data manager. Storage, homogeneity and time-series stability experiments conducted over 2.5 years showed that inter-bottle variability of the IRONAGES sample was good (<7%), although there was a decrease in iron concentration in the bottles over time (0.8–0.5 nM) before a stable value was observed. This raises questions over the suitability of sample acidification and storage.

For the complete dataset of 45 results (after excluding 3 outliers not passing the screening criteria), the mean concentration of dissolved iron in the IRONAGES sample was 0.59 ± 0.21 nM, representing a coefficient of variation (%CV) for analytical comparability ("community precision") of 36% (1s), a significant improvement over earlier exercises. Within-run precision (5–10%), inter-run precision (15%) and inter-bottle homogeneity (<7%) were much better than overall analytical comparability, implying the presence of: (1) random variability (inherent to all intercomparison exercises); (2) errors in quantification of the analytical blank; and (3) systematic inter-method variability, perhaps related to secondary sample treatment (e.g. measurement of different physicochemical fractions of iron present in seawater) in the community dataset. By grouping all results for the same method, analyses performed using flow injection-luminol chemiluminescence (with FeII detection after sample reduction) [Bowie, A.R., Achterberg, E.P., Mantoura, R.F.C., Worsfold, P.J., 1998. Determination of sub-nanomolar levels of iron in seawater using flow injection with chemiluminescence detection. Anal. Chim. Acta 361, 189–200] and flow injection-catalytic spectrophotometry (using the reagent DPD) [Measures, C.I., Yuan, J., Resing, J.A., 1995. Determination of iron in seawater by flow injection analysis using in-line preconcentration and spectrophotometric detection. Mar. Chem. 50, 3–12] gave significantly ($P=0.05$) higher dissolved iron concentrations than analyses performed using isotope dilution ICPMS [Wu, J.F., Boyle, E.A., 1998. Determination of iron in seawater by high-resolution isotope dilution inductively coupled plasma mass spectrometry after $Mg(OH)_2$ co-

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precipitation. Anal. Chim. Acta 367, 183–191]. There was, however, evidence of scatter within each method group (CV up to 59%), implying that better uniformity in procedures may be required. This paper does not identify individual data and should not be viewed as an evaluation of single laboratories. Rather it summarises the status of dissolved iron analysis in seawater by the international community at the start of the 21st century, and can be used to inform future exercises including the SAFE iron intercomparison study in the North Pacific in October 2004.

Keywords: Iron; Seawater; Determination; Intercomparison; IRONAGES; Large volume sample

1. Introduction

The last quarter century has witnessed a revolution in our understanding of trace metal distributions in the World's oceans and one element, iron, has changed our thinking more than any other (Coale et al., 1999). In order to understand the factors controlling the functioning of marine ecosystems and their effect on carbon cycling (Moore et al., 2002), it is imperative that iron is measured routinely and accurately during oceanographic expeditions. During an international symposium of SCOR-IUPAC Working Group 109 on the "Biogeochemistry of Iron in Seawater" held in Amsterdam in November 1998, it became apparent that concentrations of iron in the World's surface oceans varied over several orders of magnitude (de Baar and de Jong, 2001). The lack of rigorous intercomparison exercises, quality control of trace metal data and appropriate certified reference materials (CRMs) for sub-nanomolar concentrations of iron (the National Research Council of Canada NASS-5 solution contains 3.71 ± 0.63 nM Fe—at least tenfold greater than typical open-ocean concentrations) has meant that the scientific community has little ability to correlate these observations, and distinguish between environmental variability, analytical data quality and measurement drift. Moreover, such uncertainties in the global distribution of iron preclude the development of accurate biogeochemical models of iron limitation.

Although attempts to measure iron in seawater extend back to the 1930s (Cooper, 1935), it is recognised that modern methods began with publication of a technique based on chelation-solvent extraction followed by analysis using graphite furnace atomic absorption spectrometry (GFAAS) (Danielsson et al., 1978). Further improvements in clean sampling techniques (including not using iron hydrowires; Betzer and Pilson, 1975) were reported by Bruland et al. (1979), using a similar extraction method developed independently. The use of this analytical method resulted in reported dissolved iron concentrations in seawater decreasing by up to two orders of magnitude (Achterberg et al., 2001), and enabled oceanographers to obtain the first reliable open-ocean profiles (Gordon et al., 1982). The last two decades of the 20th century saw a great deal of interest in developing new and improved land and shipboard techniques for measuring iron in seawater, many based on portable flow injection (FI) systems (Worsfold et al., 2002); to date, at least 10 different analytical methods have been reported. Whilst errors in reported iron concentrations may result from contamination or analyte loss during sampling (an extremely challenging task on research vessels partly constructed from iron), filtration or post-collection preservation (e.g. acidification) and storage of samples, it is essential to be able to attribute differences in reported concentrations for different analytical methods using a common sampling, treatment and storage protocol.

Only two, relatively small-scale, intercomparison exercises for trace metals have previously been conducted, both somewhat unsuccessful for iron compared to other elements. During a study sponsored by the International Council for the Exploration of the Sea (Bewers et al., 1981), poor inter-laboratory precision was reported over the range 14.5–31.5 nM Fe for the analysis of acidified samples by seven different laboratories. On a 1990 Intergovernmental Oceanographic Commission baseline survey (Landing et al., 1995), three laboratories reported iron data for a single profile in the North Atlantic. Results showed up to an order of magnitude degree of variability over the concentration range 0.1–5.2 nM Fe. More recently, Measures and Vink (2001) and Bowie et al. (2003) have conducted shipboard intercomparison exercises for iron using a variety of popular analytical methods. Their results indicate that concentration offsets are due to the different sensitivities of the methods to organic and colloidal fractions of iron present in seawater, and specifically the differential extraction of these fractions during preconcentration. Bowie et al. (2004) have further argued that extended storage (>6 months) of filtered, acidified seawater samples may be necessary to enable full detection of colloidal and organic iron fractions present