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Demonstration of a standard dilution technique for standard addition calibration

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ABSTRACT

A standard dilution approach to sequential (S-SAC) and conventional (C-SAC) standard addition calibration is introduced and described theoretically. The two calibration methods have then been demonstrated experimentally for chloride measurement in seawater samples. S-SAC showed superior results for such a sample as a function of the steeper extrapolation resulting from the calibration process. The conflicting effects on S-SAC of extrapolation precision and sensitivity to intercept correction have been discussed and recommendations concerning the optimum ratio of target analyte concentration in the calibration standard to that in the unknown sample for the use of this technique have been made.

1. Introduction

Calibration is an essential part of quantification in analytical chemistry for all but primary methods [1]. A working curve approach is usually preferred because in most cases the precision obtained by interpolation of unknown measurements between fixed reference points is better than using extrapolation techniques. Extrapolation techniques for calibration, such as standard addition, are usually required when the matrix of the sample differs from that of the calibration standards and the analytical technique employed is sensitive to the matrix [2]. Both working curve calibration and conventional (or fixed volume) standard addition calibration (C-SAC) involve the preparation of a number of solutions in separate containers. Sequential (or variable volume) standard addition calibration (S-SAC) uses only one container, and relies on adding the calibration standard into the same container as the unknown sample [3]. Because of the fixed volume nature of C-SAC (comprising a fixed quantity of unknown solution and inversely proportional, variable quantities of standard solution and blank balance solution) addition of standard solution always results in an overall increase in the mass fraction of analyte in solution. However, because S-SAC involves the use of differing solution volumes (comprising a fixed quantity of unknown solution and variable quantities of standard solution) if a standard solution of lower concentration than the unknown sample is used the mass fraction of analyte in the resulting mixture may actually decrease. This theoretical 'standard dilution' condition has been postulated in previous studies on S-SAC [3] but until now never fully described or demonstrated experimentally. In situations where the concentration of the analyte is large (with respect to the modern day expectations for 'trace' analysis) it may be impracticable to use standard solutions whose concentrations are greater than that of the sample because of the upper range of instrument response, or simply because many commercial traceable standard solutions are not available for purchase at concentrations above mass fractions of about 1 mg/g. In this work we describe for the first time the practical application of the standard dilution method, here for the measurement of the composition of seawater, and discuss its potential merits over C-SAC for this application. The standard dilution method described here is quite different from the serial dilutions method (SDM) of quantification [4] which results in a calibration relationship similar in appearance. However, in SDM, a standard solution more concentrated than the unknown is first added to the sample followed by sequential dilution using solvent with zero analyte content, whereas in standard dilution S-SAC each step involves the addition of a standard solution less concentrated than the unknown.

2. Experimental

All experiments were conducted in a temperature-controlled laboratory at 20 ± 2 °C. All solutions were prepared in fully cleaned and dried (in a nitrogen flow (oxygen free nitrogen, BOC))

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polypropylene labwear (Fisher) using deionised water (18.2 MΩ cm, Milli-Q system, Millipore). All chemicals were of high purity (+99.9%, Fisher) and were prepared according to the supplier's guidelines (drying at elevated temperatures for the inorganic salts). The eluent used for the IC analysis was an aqueous solution of 11 mM Na_2CO_3 and 2 mM $NaHCO_3$. Analysis was performed with a Dionex ICS-1500 ion chromatograph (IC), a self-regenerating suppressor unit, and conductivity detection as previously described [5]. A flow rate of 1.0 ml min^{-1} was used throughout. The volume of the sample injection loop was nominally 10 μl. Each sample was measured at least in triplicate. NPL is accredited to ISO 17025 by UKAS to perform these measurements. Filtered Atlantic Standard Seawater (OSIL, UK) was diluted to bring the chloride mass concentration within the range of the ion chromatograph's conductivity cell: in this case 11.4 ± 0.2 μg/ml. A standard solution for calibration of chloride mass concentration 0.593 ± 0.012 μg/ml was prepared gravimetrically using sodium chloride. For the C-SAC (fixed volume) quantification, 4 vessels were prepared each containing a 10 ml portion of the diluted seawater. To these vessels another 9 ml of liquid was added, comprising the following in the separate vessels: 9 ml deionised water; 6 ml deionised water and 3 ml calibration standard; 3 ml deionised water and 6 ml calibration standard; and 9 ml calibration standard. For the S-SAC (variable volume) quantification, 4 vessels were prepared each containing a 10 ml portion of the diluted seawater. To these vessels calibration standard was added in the volumes 0, 3, 6 and 9 ml. Quantification was performed on a mass concentration basis, rather than on a mass fraction basis, to avoid any physical matrix effects associated with density mismatching [6]. Extrapolation and quantification were performed with NPL's XLGenline software [7], using the peak areas provided by the proprietary software (Chromeleon software, Dionex).

3. Results and discussion

3.1. Theory of standard dilution

m_s is the mass of the unknown sample, m_a is the mass of the standard solution added at each given stage, x_s is the fractional content of target analyte in the unknown sample, x_a is the fractional content of target analyte in the standard solution and, $x_{s(meas)}$ is the fractional content of target analyte in the unknown sample determined directly by extrapolation, prior to correction [3].

We also define $r = x_a/x_s$ and $k = m_s/m_a$. Furthermore, and crucially in this special case of standard dilution, we assume that $x_s > x_a$, such that $r < 1$, throughout.

The generalised calibration condition summarised by these considerations is given in Fig. 1. Consider that a sample of known mass but unknown analyte content is placed in a vessel (together with some blank solution in the case of C-SAC). This solution is then analysed and a response is obtained, yielding P_0 in Fig. 1. (We assume that in the S-SAC case it does not matter whether the solution is consumed during analysis (like ion chromatography) or the analysis is non-destructive (like stripping voltammetry). In the latter case we may consider just one analysis vessel and in the former case we consider several vessels, similar to C-SAC. A known mass of a standard solution of known analyte content is then added to the same portion of the unknown sample, together with blank solution in the case of C-SAC to equalise volumes, and a further measurement is made. Repeating this process n times, with standard solution replacing blank solution to maintain a constant total volume in the case of C-SAC and with the total volume increasing with each addition for S-SAC, yields the points $P_{n,C}$ for C-SAC and $P_{n,S}$ for S-SAC. Previous work has demonstrated the

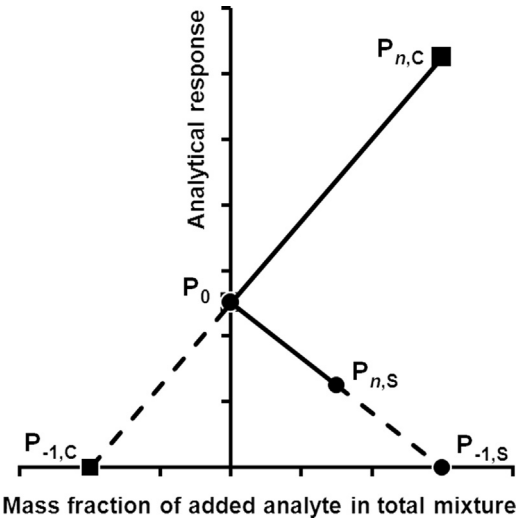

Fig. 1. Diagrammatic representation of fixed volume conventional standard addition (P_0, $P_{n,C}$ and $P_{-1,C}$) and variable volume sequential standard addition (P_0, $P_{n,S}$ and $P_{-1,S}$) calibration methods in the standard dilution scenario where the content of analyte in the sample is greater than in the standard solution ($x_s > x_a$). The solid lines represent the calibration relationship and the dashed lines the extrapolation to determine the unknown. Further explanation is given in the text.

linearity of these relationships [3]. An extrapolation of the line joining points: P_0 and $P_{n,C}$; and P_0 and $P_{n,S}$, to their intercepts with the x-axis yields $P_{-1,C}$ and $P_{-1,S}$ respectively. Note, uniquely for the standard dilution condition that the gradient of the S-SAC extrapolation is negative, as a function of the condition $x_s > x_a$, whereas the C-SAC gradient remains positive. This is because any replacement of blank solution with standard in C-SAC always increases the overall mass fraction of analyte in solution, whereas in S-SAC the addition of standard will act to reduce the overall mass fraction of analyte in solution because the volume is allowed to vary. As is shown below, this results in a shorter and more precise extrapolation for S-SAC under these conditions. We may consider for C-SAC

$$P_0 = \left(0, \frac{m_s x_s}{n m_a + m_s}\right) \tag{1}$$

$$P_{n,C} = \left(\frac{n m_a x_a}{n m_a + m_s}, \frac{n m_a x_a + m_s x_s}{n m_a + m_s}\right) \tag{2}$$

(Strictly speaking we should state that the denominator for the y-value of P_0 is $(m_s + m_b)$ since the additional material added to the original unknown sample is blank solution (of mass m_b) rather than the standard solution. However, in the n point C-SAC case we define $m_b = n m_a$; thus Eq. (1) is nevertheless correct and avoids the requirements for additional terms to be introduced). For S-SAC [3]

$$P_0 = \left(0, \frac{m_s x_s}{m_s}\right) \tag{3}$$

$$P_{n,S} = \left(\frac{n m_a x_a}{n m_a + m_s}, \frac{n m_a x_a + m_s x_s}{n m_a + m_s}\right) \tag{4}$$

Considering the generalised S-SAC strategy the real fractional content of analyte in the unknown requires a subsequent correction to the extrapolated value [3]:

$$x_s = \frac{x_a x_{s(meas)}}{x_a + x_{s(meas)}} \tag{5}$$