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The Mathematics behind Speciated Isotope Dilution Mass Spectrometry

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The Mathematics behind Speciated Isotope Dilution Mass Spectrometry

A Thesis

Presented to the Faculty

of the Department of Mathematics and Computer Science

McAnulty College and Graduate School of Liberal Arts

Duquesne University

in partial fulfillment of

the requirements for the degree of

Master of Science in Computational Mathematics

by

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The Mathematics behind Speciated Isotope Dilution Mass Spectrometry

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The Mathematics behind Speciated Isotope Dilution Mass Spectrometry

Advisor: John C. Kern II

Abstract

Speciated Isotope Dilution Mass Spectrometry (SIDMS) allows researchers to measure the concentration of species—usually elemental—in a sample by solving a system of non-linear equations. This thesis explores multiple mathematical methods to solve SIDMS equations, and compares the properties of these solution methods. Simulation analysis is conducted to provide uncertainty estimates.

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Chapter 1

Introduction

1.1 Statement of the Problem

Speciated isotope dilution mass spectrometry (SIDMS) is a newly developed method which can be used to improve accuracy in determining concentrations of chemical species in samples. It allows us to identify and determine elements in their oxidation states as well as in organometallics or other molecular forms of species [8].

An example demonstrating the usefulness of SIDMS can be found in the measurement of chromium concentration in a soil sample. Chromium exists in either a nontoxic, reduced state Chromium III (Cr(III)), or a toxic, oxidized state Chromium VI (Cr(VI)). Measuring the concentration of each of these chromium states—also and more commonly referred to as chromium species in this thesis—is complicated by the fact that inter-species conversion is an unavoidable side-effect of the measurement process. That is, the act of measuring species concentrations reduces some fraction of the original Cr(VI) to Cr(III), and oxidizes some fraction of the Cr(III) to Cr(VI). SIDMS renders inter-species conversion irrelevant by:

1. Taking into account the naturally occurring isotope ratios of chromium, and,
2. Augmenting, or spiking, the original sample with two synthesized samples.

One of these two synthesized samples is pure Cr(III), and is engineered with non-natural isotopic abundances. The other synthesized sample is pure Cr(VI), and is also engineered with non-natural isotopic abundances. By combining the two synthesized samples with the original sample (i.e. by double-spiking the original sample), the SIDMS method “builds-in” enough information to determine what the original chromium species concentrations were before inter species conversion.

In this paper, we applied SIDMS to explicitly solve for the sample concentration for each of $k = 2$ and $k = 3$ species. Some solution methods presented here generalize easily to cases where more than three species are present. A detailed discussion about SIDMS calculation is given by USWPA SW-846 Method 6800 in [9]. The method has recently been approved for the determination of the various species of metals such as Cr(III) and Cr(VI). The SIDMS method will determine the concentrations of $k = 2$ species when we solve for the four unknowns in the following system of four equations:

$$R_{50/52}^{III} = \frac{({}^{50}A_x C_x^{III} W_x + {}^{50}A_s C_s^{III} W_s^{III})(1 - \alpha) + ({}^{50}A_x C_x^{VI} W_x + {}^{50}A_s C_s^{VI} W_s^{VI})\beta}{({}^{52}A_x C_x^{III} W_x + {}^{52}A_s C_s^{III} W_s^{III})(1 - \alpha) + ({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s C_s^{VI} W_s^{VI})\beta}, \quad (1.1)$$

$$R_{53/52}^{III} = \frac{({}^{53}A_x C_x^{III} W_x + {}^{53}A_s C_s^{III} W_s^{III})(1 - \alpha) + ({}^{53}A_x C_x^{VI} W_x + {}^{53}A_s C_s^{VI} W_s^{VI})\beta}{({}^{52}A_x C_x^{III} W_x + {}^{52}A_s C_s^{III} W_s^{III})(1 - \alpha) + ({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s C_s^{VI} W_s^{VI})\beta}, \quad (1.2)$$

$$R_{50/52}^{VI} = \frac{({}^{50}A_x C_x^{III} W_x + {}^{50}A_s C_s^{III} W_s^{III})\alpha + ({}^{50}A_x C_x^{VI} W_x + {}^{50}A_s C_s^{VI} W_s^{VI})(1 - \beta)}{({}^{52}A_x C_x^{III} W_x + {}^{52}A_s C_s^{III} W_s^{III})\alpha + ({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s C_s^{VI} W_s^{VI})(1 - \beta)}, \quad (1.3)$$

$$R_{53/52}^{VI} = \frac{({}^{53}A_x C_x^{III} W_x + {}^{53}A_s C_s^{III} W_s^{III})\alpha + ({}^{53}A_x C_x^{VI} W_x + {}^{53}A_s C_s^{VI} W_s^{VI})(1 - \beta)}{({}^{52}A_x C_x^{III} W_x + {}^{52}A_s C_s^{III} W_s^{III})\alpha + ({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s C_s^{VI} W_s^{VI})(1 - \beta)}, \quad (1.4)$$

where

- $R_{50/52}^{III}$, $R_{53/52}^{III}$, $R_{50/52}^{VI}$ and $R_{53/52}^{VI}$ denote the measured isotope ratios of ^{50}Cr to ^{52}Cr of Cr(III), ^{53}Cr to ^{52}Cr of Cr(III), ^{50}Cr to ^{52}Cr of Cr(VI) and ^{53}Cr to ^{52}Cr of Cr(VI) in the spiked sample obtained from the mass spectrometer;
- $^{50}A_x$, $^{52}A_x$ and $^{53}A_x$ denote the atomic fractions of ^{50}Cr , ^{52}Cr and ^{53}Cr in the sample;
- W_x is the weight of the sample (g);
- $^{50}A_s^{III}$, $^{52}A_s^{III}$ and $^{53}A_s^{III}$ denote the atomic fractions of ^{50}Cr , ^{52}Cr and ^{53}Cr in the $^{50}\text{Cr(III)}$ spike;
- $^{50}A_s^{VI}$, $^{52}A_s^{VI}$ and $^{53}A_s^{VI}$ denote the atomic fractions of ^{50}Cr , ^{52}Cr and ^{53}Cr in the $^{53}\text{Cr(VI)}$ spike;
- C_s^{III} and C_s^{VI} denote the concentrations of Cr(III) in the $^{50}\text{Cr(III)}$ spike and Cr(VI) in the $^{53}\text{Cr(VI)}$ spike ($\mu\text{mole/g}$);
- W_s^{III} and W_s^{VI} denote the weights of $^{50}\text{Cr(III)}$ and $^{53}\text{Cr(VI)}$ spike (g);
- C_x^{III} and C_x^{VI} denote the **unknown** concentrations of Cr(III) and Cr(VI) in the sample ($\mu\text{mole/g}$);
- α and β denote the **unknown** percentages of Cr(III) oxidized to Cr(VI) and Cr(VI) reduced to Cr(III) after spiking.

These four equations are non-linear with four unknowns: C_x^{III} , C_x^{VI} , α and β . They are based on one sample, two spikes (spike A and spike B), two species (Cr(III) and Cr(VI)) and three isotopes (^{50}Cr , ^{52}Cr , and ^{53}Cr). Spike A is a ^{50}Cr -enriched spike for Cr(III) and spike B is a ^{53}Cr -enriched spike for Cr(VI). The chromium concentrations of these two spikes are known. In the original sample, the concentrations

of Cr(III) and Cr(VI) are not known, but the naturally occurring isotope proportions are well known for most elements. The sample and spikes are combined to obtain the spiked sample. Finally, a mass - spectrometer is used to measure the isotope ratios in the spiked sample (yielding the measurements of $R_{50/52}^{III}$, $R_{53/52}^{III}$, $R_{50/52}^{VI}$ and $R_{53/52}^{VI}$).

For the case of $k = 3$ species, three unknown sample concentrations and six crossover proportions will yield nine equations with nine unknowns. Letting Cr(IX) be the fictitious third species of chromium¹, and ^{54}Cr be the fourth isotope, we present below the three species SIDMS equations.

The nine unknowns C_x^{III} , C_x^{VI} , C_x^{IX} , α , β , γ , α' , β' and γ' are defined in analogous fashion to the two species case.

- C_x^{III} , C_x^{VI} , and C_x^{IX} denote the unknown concentrations of Cr(III), Cr(VI) and Cr(IX) in the sample ($\mu\text{mole/g}$);
- α , β , and γ denote the unknown percentages of Cr(III) oxidized to Cr(VI), Cr(III) oxidized to Cr(IX), and Cr(VI) oxidized to Cr(IX) after spiking;
- α' , β' , and γ' denote the unknown percentages of Cr(VI) reduced to Cr(III), Cr(IX) reduced to Cr(III), and Cr(IX) reduced to Cr(VI) after spiking.

For notational convenience, let

- $N_1 = (^{50}\text{A}_x C_x^{III} W_x + ^{50}\text{A}_s^{III} C_s^{III} W_s^{III})(1 - \alpha - \beta) + (^{50}\text{A}_x C_x^{VI} W_x + ^{50}\text{A}_s^{VI} C_s^{VI} W_s^{VI})\alpha' + (^{50}\text{A}_x C_x^{IX} W_x + ^{50}\text{A}_s^{IX} C_s^{IX} W_s^{IX})\beta'$
- $N_2 = (^{53}\text{A}_x C_x^{III} W_x + ^{53}\text{A}_s^{III} C_s^{III} W_s^{III})(1 - \alpha - \beta) + (^{53}\text{A}_x C_x^{VI} W_x + ^{53}\text{A}_s^{VI} C_s^{VI} W_s^{VI})\alpha' + (^{53}\text{A}_x C_x^{IX} W_x + ^{53}\text{A}_s^{IX} C_s^{IX} W_s^{IX})\beta'$
- $N_3 = (^{54}\text{A}_x C_x^{III} W_x + ^{54}\text{A}_s^{III} C_s^{III} W_s^{III})(1 - \alpha - \beta) + (^{54}\text{A}_x C_x^{VI} W_x + ^{54}\text{A}_s^{VI} C_s^{VI} W_s^{VI})\alpha' + (^{54}\text{A}_x C_x^{IX} W_x + ^{54}\text{A}_s^{IX} C_s^{IX} W_s^{IX})\beta'$

¹Real applications of SIDMS to three species problems include the determination of mercury species concentrations (methyl, ethyl, and inorganic)

- $D_1 = ({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III})(1 - \alpha - \beta) + ({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI})\alpha' + ({}^{52}A_x C_x^{IX} W_x + {}^{52}A_s^{IX} C_s^{IX} W_s^{IX})\beta'$.

It follows that

$$R_{50/52}^{III} = \frac{N_1}{D_1} \quad (1.5)$$

$$R_{53/52}^{III} = \frac{N_2}{D_1} \quad (1.6)$$

$$R_{54/52}^{III} = \frac{N_3}{D_1}. \quad (1.7)$$

Let

- $N_4 = ({}^{50}A_x C_x^{III} W_x + {}^{50}A_s^{III} C_s^{III} W_s^{III})\alpha + ({}^{50}A_x C_x^{IX} W_x + {}^{50}A_s^{IX} C_s^{IX} W_s^{IX})\gamma' + ({}^{50}A_x C_x^{VI} W_x + {}^{50}A_s^{VI} C_s^{VI} W_s^{VI})(1 - \gamma - \alpha')$

- $N_5 = ({}^{53}A_x C_x^{III} W_x + {}^{53}A_s^{III} C_s^{III} W_s^{III})\alpha + ({}^{53}A_x C_x^{IX} W_x + {}^{53}A_s^{IX} C_s^{IX} W_s^{IX})\gamma' + ({}^{53}A_x C_x^{VI} W_x + {}^{53}A_s^{VI} C_s^{VI} W_s^{VI})(1 - \gamma - \alpha')$

- $N_6 = ({}^{54}A_x C_x^{III} W_x + {}^{54}A_s^{III} C_s^{III} W_s^{III})\alpha + ({}^{54}A_x C_x^{IX} W_x + {}^{54}A_s^{IX} C_s^{IX} W_s^{IX})\gamma' + ({}^{54}A_x C_x^{VI} W_x + {}^{54}A_s^{VI} C_s^{VI} W_s^{VI})(1 - \gamma - \alpha')$

- $D_2 = ({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III})\alpha + ({}^{52}A_x C_x^{IX} W_x + {}^{52}A_s^{IX} C_s^{IX} W_s^{IX})\gamma' + ({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI})(1 - \gamma - \alpha')$.

It follows that

$$R_{50/52}^{VI} = \frac{N_4}{D_2} \quad (1.8)$$

$$R_{53/52}^{VI} = \frac{N_5}{D_2} \quad (1.9)$$

$$R_{54/52}^{VI} = \frac{N_6}{D_2}. \quad (1.10)$$

Let

- $N_7 = ({}^{50}A_x C_x^{III} W_x + {}^{50}A_s^{III} C_s^{III} W_s^{III})\beta + ({}^{50}A_x C_x^{VI} W_x + {}^{50}A_s^{VI} C_s^{VI} W_s^{VI})\gamma + ({}^{50}A_x C_x^{IX} W_x + {}^{50}A_s^{IX} C_s^{IX} W_s^{IX})(1 - \beta' - \gamma')$

- $N_8 = ({}^{53}A_x C_x^{III} W_x + {}^{53}A_s^{III} C_s^{III} W_s^{III})\beta + ({}^{53}A_x C_x^{VI} W_x + {}^{53}A_s^{VI} C_s^{VI} W_s^{VI})\gamma + ({}^{53}A_x C_x^{IX} W_x + {}^{53}A_s^{IX} C_s^{IX} W_s^{IX})(1 - \beta' - \gamma')$
- $N_9 = ({}^{54}A_x C_x^{III} W_x + {}^{54}A_s^{III} C_s^{III} W_s^{III})\beta + ({}^{54}A_x C_x^{VI} W_x + {}^{54}A_s^{VI} C_s^{VI} W_s^{VI})\gamma + ({}^{54}A_x C_x^{IX} W_x + {}^{54}A_s^{IX} C_s^{IX} W_s^{IX})(1 - \beta' - \gamma')$
- $D_3 = ({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III})\beta + ({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI})\gamma + ({}^{52}A_x C_x^{IX} W_x + {}^{52}A_s^{IX} C_s^{IX} W_s^{IX})(1 - \beta' - \gamma')$.

It follows that

$$R_{50/52}^{IX} = \frac{N_7}{D_3} \quad (1.11)$$

$$R_{53/52}^{IX} = \frac{N_8}{D_3} \quad (1.12)$$

$$R_{54/52}^{IX} = \frac{N_9}{D_3}. \quad (1.13)$$

Method 6800 can also be applied to the general case of k species. Based on the cases of $k = 2$ species and $k = 3$ species, it is clear that analyzing k species will yield a total of k^2 unknowns, including k concentrations and $k(k - 1)$ inter-conversion parameters, as well as k^2 non-linear equations.

Chapter 2

Solution Methods

2.1 Deterministic Method

Directly solving the system of equations (1.1) – (1.4) is possible with the help of computer software. MAPLE software produces the solution for the unknowns C_x^{III} , C_x^{VI} , α and β , and is shown in Appendix A. However, in cases where three or more species are involved, MAPLE is not able to provide a deterministic solution. Thus, the deterministic solution method is applied only in cases where exactly two species are considered. The deterministic solutions given in Appendix A have not been recognized before this thesis. The “traditional” approach to solving the SIDMS equations — according to an overwhelming majority of SIDMS literature ([8], [4], [6], [13]) — is the iterative method presented in the following section.

2.2 Iterative Method

First, consider the case of $k = 2$ species. In order to simplify (1.1) – (1.4), we let $C_x^{III}W_x = N_x^{III}$, $C_x^{VI}W_x = N_x^{VI}$, $C_s^{III}W_s^{III} = N_s^{III}$, and $C_s^{VI}W_s^{VI} = N_s^{VI}$.

Before the first iteration, we set the values of N_x^{VI} and α equal to 0 since their

starting values can be chosen arbitrarily¹. Next, rewrite (1.1) and (1.2) as linear equations in N_x^{III} and β :

$$(1 - \alpha)(R_{50/52}^{III} {}^{52}A_x - {}^{50}A_x)N_x^{III} + [R_{50/52}^{III}({}^{52}A_x N_x^{VI} + {}^{52}A_s^{VI} N_s^{VI}) - ({}^{50}A_x N_x^{VI} + {}^{50}A_s^{VI} N_s^{VI})]\beta = (-R_{50/52}^{III} {}^{52}A_s^{III} + {}^{50}A_s^{III})N_s^{III}(1 - \alpha) \quad (2.1)$$

$$(1 - \alpha)(R_{53/52}^{III} {}^{52}A_x - {}^{53}A_x)N_x^{III} + [R_{53/52}^{III}({}^{52}A_x N_x^{VI} + {}^{52}A_s^{VI} N_s^{VI}) - ({}^{53}A_x N_x^{VI} + {}^{53}A_s^{VI} N_s^{VI})]\beta = (-R_{53/52}^{III} {}^{52}A_s^{III} + {}^{53}A_s^{III})N_s^{III}(1 - \alpha). \quad (2.2)$$

To make the linearity of (2.1) and (2.2) more transparent, let

- $A_1 = (1 - \alpha)(R_{50/52}^{III} {}^{52}A_x - {}^{50}A_x)$
- $B_1 = R_{50/52}^{III}({}^{52}A_x N_x^{VI} + {}^{52}A_s^{VI} N_s^{VI}) - ({}^{50}A_x N_x^{VI} + {}^{50}A_s^{VI} N_s^{VI})$
- $C_1 = (-R_{50/52}^{III} {}^{52}A_s^{III} + {}^{50}A_s^{III})N_s^{III}(1 - \alpha)$
- $A_2 = (1 - \alpha)(R_{53/52}^{III} {}^{52}A_x - {}^{53}A_x)$
- $B_2 = R_{53/52}^{III}({}^{52}A_x N_x^{VI} + {}^{52}A_s^{VI} N_s^{VI}) - ({}^{53}A_x N_x^{VI} + {}^{53}A_s^{VI} N_s^{VI})$
- $C_2 = (-R_{53/52}^{III} {}^{52}A_s^{III} + {}^{53}A_s^{III})N_s^{III}(1 - \alpha).$

Then (2.1) and (2.2) can be rewritten as the following:

$$A_1 N_x^{III} + B_1 \beta = C_1 \quad (2.3)$$

$$A_2 N_x^{III} + B_2 \beta = C_2. \quad (2.4)$$

Solving these two equations for the unknowns N_x^{III} and β gives:

$$N_x^{III} = \frac{B_2 C_1 - B_1 C_2}{A_1 B_2 - A_2 B_1}, \quad \beta = \frac{A_1 C_2 - A_2 C_1}{A_1 B_2 - A_2 B_1}. \quad (2.5)$$

¹Concentration starting values should be non-negative and proportion starting values should be contained in $[0,1]$.

Use the two solutions from (1.3) and (1.4), rewritten here to be linear in N_x^{VI} and α :

$$(1 - \beta)(R_{50/52}^{VI} {}^{52}A_x - {}^{50}A_x)N_x^{VI} + [R_{50/52}^{VI}({}^{52}A_x N_x^{III} + {}^{52}A_s^{III} N_s^{III}) - ({}^{50}A_x N_x^{III} + {}^{50}A_s^{III} N_s^{III})]\alpha = (-R_{50/52}^{VI} {}^{52}A_s^{VI} + {}^{50}A_s^{VI})N_s^{VI}(1 - \beta) \quad (2.6)$$

$$(1 - \beta)(R_{53/52}^{VI} {}^{52}A_x - {}^{53}A_x)N_x^{VI} + [R_{53/52}^{VI}({}^{52}A_x N_x^{III} + {}^{52}A_s^{III} N_s^{III}) - ({}^{53}A_x N_x^{III} + {}^{53}A_s^{III} N_s^{III})]\alpha = (-R_{53/52}^{VI} {}^{52}A_s^{VI} + {}^{53}A_s^{VI})N_s^{VI}(1 - \beta). \quad (2.7)$$

In analogous fashion to (2.3) and (2.4), simplify the notation for the coefficients of N_x^{VI} and α to obtain a streamlined version of (2.6) and (2.7)

$$A_3 N_x^{VI} + B_3 \alpha = C_3 \quad (2.8)$$

$$A_4 N_x^{VI} + B_4 \alpha = C_4. \quad (2.9)$$

Solving (2.8) and (2.9) for the unknowns N_x^{VI} and α gives

$$N_x^{VI} = \frac{B_4 C_3 - B_3 C_4}{A_3 B_4 - A_4 B_3}, \quad \alpha = \frac{A_3 C_4 - A_4 C_3}{A_3 B_4 - A_4 B_3}, \quad (2.10)$$

where

- $A_3 = (1 - \beta)(R_{50/52}^{VI} {}^{52}A_x - {}^{50}A_x)$
- $B_3 = R_{50/52}^{VI}({}^{52}A_x N_x^{III} + {}^{52}A_s^{III} N_s^{III}) - ({}^{50}A_x N_x^{III} + {}^{50}A_s^{III} N_s^{III})$
- $C_3 = (-R_{50/52}^{VI} {}^{52}A_s^{VI} + {}^{50}A_s^{VI})N_s^{VI}(1 - \beta)$
- $A_4 = (1 - \beta)(R_{53/52}^{VI} {}^{52}A_x - {}^{53}A_x)$
- $B_4 = R_{53/52}^{VI}({}^{52}A_x N_x^{III} + {}^{52}A_s^{III} N_s^{III}) - ({}^{53}A_x N_x^{III} + {}^{53}A_s^{III} N_s^{III})$
- $C_4 = (-R_{53/52}^{VI} {}^{52}A_s^{VI} + {}^{53}A_s^{VI})N_s^{VI}(1 - \beta).$

Use the two solutions in (2.10) to re-compute the coefficients of N_x^{III} and β in (2.3) and (2.4). Solve for N_x^{III} and β , and use these solutions to re-compute the coefficients of N_x^{VI} and α in (2.8) and (2.9). Repeat these calculations until the four unknowns converge to constant values. These values will be an approximation to the solution to the system of four non-linear equations. Details of the convergence properties of the iterative method are given in Chapter 3.

The iterative method can also be used to solve for the unknown concentrations of three (or more) species. For the three species case, rewrite equations (1.5) to (1.13) as linear equations in three of the nine unknowns; each of the nine equations treats six of the unknown parameters as fixed. Letting $N_s^{III} = C_s^{III}W_s^{III}$, $N_s^{VI} = C_s^{VI}W_s^{VI}$, $N_s^{IX} = C_s^{IX}W_s^{IX}$, $N_x^{III} = C_x^{III}W_x$, $N_x^{VI} = C_x^{VI}W_x$, $N_x^{IX} = C_x^{IX}W_x$ converts (1.5) – (1.7) to equations which are linear with respect to N_x^{III} , α' , and β' :

$$A_1N_x^{III} + B_1\alpha' + C_1\beta' = D_1 \quad (2.11)$$

$$A_2N_x^{III} + B_2\alpha' + C_2\beta' = D_2 \quad (2.12)$$

$$A_3N_x^{III} + B_3\alpha' + C_3\beta' = D_3; \quad (2.13)$$

(1.8) – (1.10) to equations which are linear with respect to N_x^{VI} , α , and γ' :

$$A_4N_x^{VI} + B_4\alpha + C_4\gamma' = D_4 \quad (2.14)$$

$$A_5N_x^{VI} + B_5\alpha + C_5\gamma' = D_5 \quad (2.15)$$

$$A_6N_x^{VI} + B_6\alpha + C_6\gamma' = D_6; \quad (2.16)$$

and (1.11) – (1.13) to equations which are linear with respect to N_x^{IX} , β , and γ :

$$A_7N_x^{IX} + B_7\beta + C_7\gamma = D_7 \quad (2.17)$$

$$A_8 N_x^{IX} + B_8 \beta + C_8 \gamma = D_8 \quad (2.18)$$

$$A_9 N_x^{IX} + B_9 \beta + C_9 \gamma = D_9. \quad (2.19)$$

The coefficients and constants in these nine equations (2.11) – (2.19) are given by:

- $A_1 = (1 - \alpha - \beta)(R_{50/52}^{III} {}^{52}A_x - {}^{50}A_x)$
- $B_1 = R_{50/52}^{III}({}^{52}A_x N_x^{VI} + {}^{52}A_s^{VI} N_s^{VI}) - ({}^{50}A_x N_x^{VI} + {}^{50}A_s^{VI} N_s^{VI})$
- $C_1 = R_{50/52}^{III}({}^{52}A_x N_x^{IX} + {}^{52}A_s^{IX} N_s^{IX}) - ({}^{50}A_x N_x^{IX} + {}^{50}A_s^{IX} N_s^{IX})$
- $D_1 = (-R_{50/52}^{III} {}^{52}A_s^{III} + {}^{50}A_s^{III})N_s^{III}(1 - \alpha - \beta)$
- $A_2 = (1 - \alpha - \beta)(R_{53/52}^{III} {}^{52}A_x - {}^{53}A_x)$
- $B_2 = R_{53/52}^{III}({}^{52}A_x N_x^{VI} + {}^{52}A_s^{VI} N_s^{VI}) - ({}^{53}A_x N_x^{VI} + {}^{53}A_s^{VI} N_s^{VI})$
- $C_2 = R_{53/52}^{III}({}^{52}A_x N_x^{IX} + {}^{52}A_s^{IX} N_s^{IX}) - ({}^{53}A_x N_x^{IX} + {}^{53}A_s^{IX} N_s^{IX})$
- $D_2 = (-R_{53/52}^{III} {}^{52}A_s^{III} + {}^{53}A_s^{III})N_s^{III}(1 - \alpha - \beta)$
- $A_3 = (1 - \alpha - \beta)(R_{54/52}^{III} {}^{52}A_x - {}^{54}A_x)$
- $B_3 = R_{54/52}^{III}({}^{52}A_x N_x^{VI} + {}^{52}A_s^{VI} N_s^{VI}) - ({}^{54}A_x N_x^{VI} + {}^{54}A_s^{VI} N_s^{VI})$
- $C_3 = R_{54/52}^{III}({}^{52}A_x N_x^{IX} + {}^{52}A_s^{IX} N_s^{IX}) - ({}^{54}A_x N_x^{IX} + {}^{54}A_s^{IX} N_s^{IX})$
- $D_3 = (-R_{54/52}^{III} {}^{52}A_s^{III} + {}^{54}A_s^{III})N_s^{III}(1 - \alpha - \beta)$
- $A_4 = (1 - \gamma - \alpha')(R_{50/52}^{VI} {}^{52}A_x - {}^{50}A_x)$
- $B_4 = R_{50/52}^{VI}({}^{52}A_x N_x^{III} + {}^{52}A_s^{III} N_s^{VI}) - ({}^{50}A_x N_x^{III} + {}^{50}A_s^{III} N_s^{III})$
- $C_4 = R_{50/52}^{VI}({}^{52}A_x N_x^{IX} + {}^{52}A_s^{IX} N_s^{IX}) - ({}^{50}A_x N_x^{IX} + {}^{50}A_s^{IX} N_s^{IX})$
- $D_4 = (-R_{50/52}^{VI} {}^{52}A_s^{VI} + {}^{50}A_s^{VI})N_s^{VI}(1 - \gamma - \alpha')$
- $A_5 = (1 - \gamma - \alpha')(R_{50/52}^{VI} {}^{52}A_x - {}^{53}A_x)$

- $B_5 = R_{53/52}^{VI} ({}^{52}A_x N_x^{III} + {}^{52}A_s^{III} N_s^{VI}) - ({}^{53}A_x N_x^{III} + {}^{53}A_s^{III} N_s^{III})$
- $C_5 = R_{53/52}^{VI} ({}^{52}A_x N_x^{IX} + {}^{52}A_s^{IX} N_s^{IX}) - ({}^{53}A_x N_x^{IX} + {}^{53}A_s^{IX} N_s^{IX})$
- $D_5 = (-R_{53/52}^{VI} {}^{52}A_s^{VI} + {}^{53}A_s^{VI}) N_s^{VI} (1 - \gamma - \alpha')$
- $A_6 = (1 - \gamma - \alpha') (R_{54/52}^{VI} {}^{52}A_x - {}^{54}A_x)$
- $B_6 = R_{54/52}^{VI} ({}^{52}A_x N_x^{III} + {}^{52}A_s^{III} N_s^{VI}) - ({}^{54}A_x N_x^{III} + {}^{54}A_s^{III} N_s^{III})$
- $C_6 = R_{54/52}^{VI} ({}^{52}A_x N_x^{IX} + {}^{52}A_s^{IX} N_s^{IX}) - ({}^{54}A_x N_x^{IX} + {}^{54}A_s^{IX} N_s^{IX})$
- $D_6 = (-R_{54/52}^{VI} {}^{52}A_s^{VI} + {}^{54}A_s^{VI}) N_s^{VI} (1 - \gamma - \alpha')$
- $A_7 = (1 - \beta' - \gamma') (R_{50/52}^{IX} {}^{52}A_x - {}^{50}A_x)$
- $B_7 = R_{50/52}^{IX} ({}^{52}A_x N_x^{III} + {}^{52}A_s^{III} N_s^{III}) - ({}^{50}A_x N_x^{III} + {}^{50}A_s^{III} N_s^{III})$
- $C_7 = R_{50/52}^{IX} ({}^{52}A_x N_x^{VI} + {}^{52}A_s^{IX} N_s^{VI}) - ({}^{50}A_x N_x^{VI} + {}^{50}A_s^{VI} N_s^{VI})$
- $D_7 = (-R_{50/52}^{IX} {}^{52}A_s^{IX} + {}^{50}A_s^{IX}) N_s^{IX} (1 - \beta' - \gamma')$
- $A_8 = (1 - \beta' - \gamma') (R_{53/52}^{IX} {}^{52}A_x - {}^{53}A_x)$
- $B_8 = R_{53/52}^{IX} ({}^{52}A_x N_x^{III} + {}^{52}A_s^{III} N_s^{III}) - ({}^{53}A_x N_x^{III} + {}^{53}A_s^{III} N_s^{III})$
- $C_8 = R_{53/52}^{IX} ({}^{52}A_x N_x^{VI} + {}^{52}A_s^{IX} N_s^{VI}) - ({}^{53}A_x N_x^{VI} + {}^{53}A_s^{VI} N_s^{VI})$
- $D_8 = (-R_{53/52}^{IX} {}^{52}A_s^{IX} + {}^{53}A_s^{IX}) N_s^{IX} (1 - \beta' - \gamma')$
- $A_9 = (1 - \beta' - \gamma') (R_{54/52}^{IX} {}^{52}A_x - {}^{54}A_x)$
- $B_9 = R_{54/52}^{IX} ({}^{52}A_x N_x^{III} + {}^{52}A_s^{III} N_s^{III}) - ({}^{54}A_x N_x^{III} + {}^{54}A_s^{III} N_s^{III})$
- $C_9 = R_{54/52}^{IX} ({}^{52}A_x N_x^{VI} + {}^{52}A_s^{IX} N_s^{VI}) - ({}^{54}A_x N_x^{VI} + {}^{54}A_s^{VI} N_s^{VI})$
- $D_9 = (-R_{54/52}^{IX} {}^{52}A_s^{IX} + {}^{54}A_s^{IX}) N_s^{IX} (1 - \beta' - \gamma')$

Solving (2.11)-(2.13) yields:

$$N_x^{III} = \frac{-D_1B_2C_3 + D_1B_3C_2 - B_1D_3C_2 + B_1C_3D_2 - C_1B_3D_2 + C_1B_2D_3}{-A_1B_2C_3 + A_1B_3C_2 - B_3A_2C_1 - A_3B_1C_2 + B_2A_3C_1 + A_2B_1C_3} \quad (2.20)$$

$$\alpha' = \frac{A_1D_3C_2 - A_1C_3D_2 + A_3C_1D_2 + C_3A_2D_1 - D_3A_2C_1 - A_3D_1C_2}{-A_1B_2C_3 + A_1B_3C_2 - B_3A_2C_1 - A_3B_1C_2 + B_2A_3C_1 + A_2B_1C_3} \quad (2.21)$$

$$\beta' = \frac{A_1B_3D_2 + A_2B_1D_3 - B_3A_2D_1 - A_1B_2D_3 - A_3B_1D_2 + B_2A_3D_1}{-A_1B_2C_3 + A_1B_3C_2 - B_3A_2C_1 - A_3B_1C_2 + B_2A_3C_1 + A_2B_1C_3}. \quad (2.22)$$

Solving (2.14)-(2.16) yields:

$$N_x^{VI} = \frac{-B_4C_5D_6 + B_4C_6D_5 + B_5C_4D_6 + C_5B_6D_4 - C_6B_5D_4 - B_6C_4D_5}{-B_4C_5A_6 + B_4C_6A_5 + B_5C_4A_6 + C_5B_6A_4 - C_6B_5A_4 - B_6C_4A_5} \quad (2.23)$$

$$\alpha = \frac{-D_4C_5A_6 + D_4C_6A_5 + A_4C_5D_6 - A_4C_6D_5 - C_4A_5D_6 + C_4D_5A_6}{-B_4C_5A_6 + B_4C_6A_5 + B_5C_4A_6 + C_5B_6A_4 - C_6B_5A_4 - B_6C_4A_5} \quad (2.24)$$

$$\gamma' = \frac{B_4A_5D_6 - B_4D_5A_6 + D_5B_6A_4 - A_5B_6D_4 - B_5A_4D_6 + B_5D_4A_6}{-B_4C_5A_6 + B_4C_6A_5 + B_5C_4A_6 + C_5B_6A_4 - C_6B_5A_4 - B_6C_4A_5}. \quad (2.25)$$

Solving (2.17)-(2.19) yields:

$$N_x^{IX} = \frac{-B_7D_8C_9 + B_7C_8D_9 - C_8B_9D_7 + D_8B_9C_7 - B_8C_7D_9 + B_8D_7C_9}{-B_8A_9C_7 + B_8A_7C_9 - A_7B_9C_8 - B_7A_8C_9 + A_9B_7C_8 + B_9A_8C_7} \quad (2.26)$$

$$\beta = \frac{-D_8A_9C_7 + D_8A_7C_9 + A_8C_7D_9 - A_8D_7C_9 - C_8A_7D_9 + C_8A_9D_7}{-B_8A_9C_7 + B_8A_7C_9 - A_7B_9C_8 - B_7A_8C_9 + A_9B_7C_8 + B_9A_8C_7} \quad (2.27)$$

$$\gamma = \frac{B_8A_7D_9 + B_9A_8D_7 - A_7B_9D_8 - B_8A_9D_7 - B_7A_8D_9 + A_9B_7D_8}{-B_8A_9C_7 + B_8A_7C_9 - A_7B_9C_8 - B_7A_8C_9 + A_9B_7C_8 + B_9A_8C_7}. \quad (2.28)$$

The starting values of the six unknowns N_x^{VI} , N_x^{IX} , α , β , γ , γ' are arbitrarily chosen and the three equations (2.20) – (2.22) are used to calculate the estimates of N_x^{III} , α' and β' . Then (2.23) – (2.25) are used to calculate the estimates of N_x^{VI} , α and γ' given the starting values of N_x^{IX} , β and γ and the estimates of N_x^{III} , α' and β' from the previous step. Finally, (2.26) – (2.28) are used to obtain the estimates of N_x^{IX} , β and γ given the estimates of N_x^{III} , α' , β' , N_x^{VI} , α and γ' from the previous two steps.

The three steps can be iterated until convergence². The result is an approximation of the solutions to (2.11) – (2.19).

2.3 Matrix Method

The matrix method was originally developed by Bret Larget in 1995 and is unpublished. It approaches the task of solving for the unknown concentrations and crossover parameters from a different perspective than the deterministic or iterative settings. The method is presented in the following two and three species scenarios.

2.3.1 Two Species Matrix Method

As in SIDMS protocol, prepare two isotopic spikes representing each of the two species. Spike A is a ^{50}Cr –enriched spike for Cr(III) and spike B is a ^{53}Cr –enriched spike for Cr(VI).

Let ω be the vector that represents the atomic masses of each isotope, then for spike A, define

- \mathbf{a} as the vector that represents the atomic proportion of each isotope in spike A;
- c_a as the concentration of chromium in spike A (mg/mL);
- v_a as the volume of spike A (μL).

Then the total number of moles of chromium in spike A is

$$m_a = \frac{c_a v_a \times (10^{-3} \text{mL} / \mu\text{L})}{\mathbf{a}^T \cdot \omega}.$$

For spike B, define

²The iterations will be stopped if the change in the nine parameter estimates does not exceed some pre-specified tolerance.

- \mathbf{b} as the vector that represents the atomic proportion of each isotope in spike B;
- c_b as the concentration of chromium in spike B (mg/mL);
- v_b as the volume of spike B (μL).

Similarly, we obtain the total number of moles of chromium in spike B:

$$m_b = \frac{c_b v_b \times (10^{-3} \text{mL}/\mu\text{L})}{\mathbf{b}^T \cdot \boldsymbol{\omega}}.$$

For the original sample, define

- \mathbf{n} as the vector that represents the natural atomic proportion of each isotope;
- c_n as the **unknown** concentration of chromium in the sample (mg/mL);
- v_n as the volume of the sample (μL).

Then the total number of moles of chromium in original sample is

$$m_n = \frac{c_n v_n \times (10^{-3} \text{mL}/\mu\text{L})}{\mathbf{n}^T \cdot \boldsymbol{\omega}}.$$

The three sources are combined in order to find the concentration of each species in the original sample. First, let the vectors \mathbf{x} and \mathbf{y} represent the observed proportions of each isotope for Cr(III) and Cr(VI) after spiking, respectively. Furthermore, define the following:

- p is the percentage of the Cr(III) in the sample;
- q is the percentage of Cr(III) oxidized to Cr(VI) at the time of measurement;
- r is the percentage of Cr(VI) reduced to Cr(III) at the time of measurement.

Then the total number of moles of Cr(III) at the time of measurement is

$$(1 - q)m_a + rm_b + ((1 - q)p + r(1 - p))m_n$$

and the total number of moles of Cr(VI) at the time of measurement is

$$qm_a + (1 - r)m_b + (qp + (1 - r)(1 - p))m_n.$$

Assuming there is no measurement error, and the crossover percentage is the same for each source, the measured proportions are described by the following two equations:

$$((1 - q)m_a + rm_b + ((1 - q)p + r(1 - p))m_n)\mathbf{x} = (1 - q)m_a\mathbf{a} + rm_b\mathbf{b} + ((1 - q)p + r(1 - p))m_n\mathbf{n} \quad (2.29)$$

$$(qm_a + (1 - r)m_b + (qp + (1 - r)(1 - p))m_n)\mathbf{y} = qm_a\mathbf{a} + (1 - r)m_b\mathbf{b} + (qp + (1 - r)(1 - p))m_n\mathbf{n} \quad (2.30)$$

Dividing both sides of (2.29) by the total number of moles of Cr(III), and letting

$$\alpha = \frac{(1 - q)m_a}{(1 - q)m_a + rm_b + ((1 - q)p + r(1 - p))m_n},$$

$$\beta = \frac{rm_b}{(1 - q)m_a + rm_b + ((1 - q)p + r(1 - p))m_n},$$

we obtain

$$\mathbf{x} = \alpha\mathbf{a} + \beta\mathbf{b} + (1 - \alpha - \beta)\mathbf{n}. \quad (2.31)$$

Similarly, dividing both sides of (2.30) by the total number of moles of Cr(VI), and letting

$$\alpha^* = \frac{qm_a}{qm_a + (1 - r)m_b + (qp + (1 - r)(1 - p))m_n}$$

$$\beta^* = \frac{(1-r)m_b}{qm_a + (1-r)m_b + (qp + (1-r)(1-p))m_n},$$

then we have

$$\mathbf{y} = \alpha^* \mathbf{a} + \beta^* \mathbf{b} + (1 - \alpha^* - \beta^*) \mathbf{n}. \quad (2.32)$$

Rewrite (2.31) and (2.32) as follows:

$$(\mathbf{x} - \mathbf{n}) = \alpha(\mathbf{a} - \mathbf{n}) + \beta(\mathbf{b} - \mathbf{n}) \quad (2.33)$$

$$(\mathbf{y} - \mathbf{n}) = \alpha^*(\mathbf{a} - \mathbf{n}) + \beta^*(\mathbf{b} - \mathbf{n}). \quad (2.34)$$

Furthermore, rewrite (2.33) and (2.34) using the matrix form as

$$(\mathbf{x} - \mathbf{n}) = \begin{bmatrix} \mathbf{a} - \mathbf{n} & \mathbf{b} - \mathbf{n} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \quad (2.35)$$

and

$$(\mathbf{y} - \mathbf{n}) = \begin{bmatrix} \mathbf{a} - \mathbf{n} & \mathbf{b} - \mathbf{n} \end{bmatrix} \begin{bmatrix} \alpha^* \\ \beta^* \end{bmatrix}. \quad (2.36)$$

Using the method of linear regression on (2.35) and (2.36) to solve for α , β , α^* and β^* gives:

$$\begin{bmatrix} \alpha \\ \beta \end{bmatrix} = (X^T X)^{-1} X^T (\mathbf{x} - \mathbf{n}) \quad (2.37)$$

and

$$\begin{bmatrix} \alpha^* \\ \beta^* \end{bmatrix} = (X^T X)^{-1} X^T (\mathbf{y} - \mathbf{n}), \quad (2.38)$$

where X represents the 3×2 matrix with columns $(\mathbf{a} - \mathbf{n})$ and $(\mathbf{b} - \mathbf{n})$.

Using (2.29) and (2.30) can provide the following equations

$$\frac{(1-q)m_a}{rm_b} = \frac{\alpha}{\beta}, \quad \frac{qm_a}{(1-r)m_b} = \frac{\alpha^*}{\beta^*}.$$

Rewriting these two equations in matrix form yields:

$$\begin{bmatrix} \beta m_a & \alpha m_b \\ \beta^* m_a & \alpha^* m_b \end{bmatrix} \begin{bmatrix} q \\ r \end{bmatrix} = \begin{bmatrix} \beta m_a \\ \alpha^* m_b \end{bmatrix}, \quad (2.39)$$

and solving (2.39) for q and r gives:

$$\begin{bmatrix} q \\ r \end{bmatrix} = \frac{1}{(\alpha^* \beta - \alpha \beta^*) m_a m_b} \begin{bmatrix} \alpha^* m_b & -\alpha m_b \\ -\beta^* m_a & \beta m_a \end{bmatrix} \begin{bmatrix} \beta m_a \\ \alpha^* m_b \end{bmatrix} = \begin{bmatrix} \frac{\alpha^* (\beta m_a - \alpha m_b)}{(\alpha^* \beta - \alpha \beta^*) m_a} \\ \frac{\beta (\beta^* m_a - \alpha^* m_b)}{(\alpha \beta^* - \alpha^* \beta) m_b} \end{bmatrix}. \quad (2.40)$$

That is,

$$q = \frac{\alpha^* (\beta m_a - \alpha m_b)}{(\alpha^* \beta - \alpha \beta^*) m_a}, \quad r = \frac{\beta (\beta^* m_a - \alpha^* m_b)}{(\alpha \beta^* - \alpha^* \beta) m_b}.$$

From (2.29) and (2.30), it is given that the ratio of the total number of moles of Cr(III) from the natural sample to the total number of moles from spike A is equal to the ratio of $1 - \alpha - \beta$ to α . That is

$$\frac{1 - \alpha - \beta}{\alpha} = \frac{((1-q)p + r(1-p))m_n}{(1-q)m_a}. \quad (2.41)$$

Similarly, the ratio of the total number of moles of Cr(VI) from the natural sample to the total number of moles from spike B is equal to the ratio of $1 - \alpha^* - \beta^*$ to β^* .

That is

$$\frac{1 - \alpha^* - \beta^*}{\beta^*} = \frac{(qp + (1-r)(1-p))m_n}{(1-r)m_b}. \quad (2.42)$$

Then the total number of moles of species Cr(III) and Cr(VI) in the natural sample

is determined by the following equation:

$$m_n = \frac{1 - \alpha - \beta}{\alpha}(1 - q)m_a + \frac{1 - \alpha^* - \beta^*}{\beta^*}(1 - r)m_b. \quad (2.43)$$

Solving (2.41) for p gives:

$$p = \frac{(1 - \alpha - \beta)(1 - q)m_a - \alpha r m_n}{\alpha(1 - q - r)m_n}. \quad (2.44)$$

Thus the concentration of Cr(III) in the sample is equal to $pc_n = (pm_n(n^T \cdot \omega))/(v_n \times (10^{-3}mL/\mu L))$ and the concentration of Cr(VI) in the sample is equal to $(1 - p)c_n = ((1 - p)m_n(n^T \cdot \omega))/(v_n \times (10^{-3}mL/\mu L))$.

2.3.2 Three Species Matrix Method

Having established the matrix solution method for the case of two species, defining this method for three species follows in analogous fashion. First, define the following:

- \vec{x} , \vec{y} and \vec{z} denote the observed proportions of each isotope for Cr(III), Cr(VI) and Cr(IX) after spiking;
- p_1 and p_2 denote the sample proportions of Cr(III) and Cr(VI) at the time of spiking;
- q_{12} and q_{13} denote the proportions of the Cr(III) at the time of spiking that changes to Cr(VI) and Cr(IX) at the time of measurement, for all sources;
- r_{21} and r_{23} denote the proportions of the Cr(VI) at the time of spiking that changes to Cr(III) and Cr(IX) at the time of measurement, for all sources;
- s_{31} and s_{32} denote the proportions of the Cr(IX) at the time of spiking that changes to Cr(III) and Cr(VI) at the time of measurement, for all sources;

- m_a, m_b, m_c and m_n represent the total number of moles of chromium in spike A, spike B, spike C, and the natural sample;
- A, B and C represent the total number of moles of Cr(III), Cr(VI) and Cr(IX) at the time of measurement;
- $\vec{a}, \vec{b}, \vec{c}$ and \vec{n} are the vectors representing the atomic proportions of each isotope in spike A, spike B, spike C, and the natural sample;

Then the total number of moles of Cr(III) at the time of measurement is $(1 - q_{12} - q_{13})m_a + r_{21}m_b + s_{31}m_c + [(1 - q_{12} - q_{13})p_1 + r_{21}p_2 + s_{31}(1 - p_1 - p_2)]m_n$, the total number of moles of Cr(VI) at the time of measurement is $q_{12}m_a + (1 - r_{21} - r_{23})m_b + s_{32}m_c + [q_{12}p_1 + (1 - r_{21} - r_{23})p_2 + s_{32}(1 - p_1 - p_2)]m_n$, and the total number of moles of Cr(IX) at the time of measurement is $q_{13}m_a + r_{23}m_b + (1 - s_{31} - s_{32})m_c + [q_{13}p_1 + r_{23}p_2 + (1 - s_{31} - s_{32})(1 - p_1 - p_2)]m_n$.

Then the measured proportions are described by the following equations:

$$A\vec{x} = (1 - q_{12} - q_{13})m_a\vec{a} + r_{21}m_b\vec{b} + s_{31}m_c\vec{c} + [(1 - q_{12} - q_{13})p_1 + r_{21}p_2 + s_{31}(1 - p_1 - p_2)]m_n\vec{n} \quad (2.45)$$

$$B\vec{y} = q_{12}m_a\vec{a} + (1 - r_{21} - r_{23})m_b\vec{b} + s_{32}m_c\vec{c} + [q_{12}p_1 + (1 - r_{21} - r_{23})p_2 + s_{32}(1 - p_1 - p_2)]m_n\vec{n} \quad (2.46)$$

$$C\vec{z} = q_{13}m_a\vec{a} + r_{23}m_b\vec{b} + (1 - s_{31} - s_{32})m_c\vec{c} + [q_{13}p_1 + r_{23}p_2 + (1 - s_{31} - s_{32})(1 - p_1 - p_2)]m_n\vec{n}. \quad (2.47)$$

Equations (2.45) – (2.47) assume there is no measurement error, and the crossover proportion is the same for each source. Dividing both sides of (2.45) by A, dividing both sides of (2.46) by B, dividing both sides of (2.47) by C, and defining $\alpha, \beta, \gamma, \alpha', \beta', \gamma', \alpha'', \beta'', \gamma''$ as the proportions of, respectively, Cr(III) from spike A, Cr(III) from spike B, Cr(III) from spike C, Cr(VI) from spike A, Cr(VI) from spike B, Cr(VI) from spike C, Cr(IX) from spike A, Cr(IX) from spike B, Cr(IX) from spike C at the

time of measurement give the following three equations:

$$\vec{x} = \alpha\vec{a} + \beta\vec{b} + \gamma\vec{c} + (1 - \alpha - \beta - \gamma)\vec{n},$$

$$\vec{y} = \alpha'\vec{a} + \beta'\vec{b} + \gamma'\vec{c} + (1 - \alpha' - \beta' - \gamma')\vec{n},$$

$$\vec{z} = \alpha''\vec{a} + \beta''\vec{b} + \gamma''\vec{c} + (1 - \alpha'' - \beta'' - \gamma'')\vec{n}.$$

Rewriting these equations gives:

$$(\vec{x} - \vec{n}) = \alpha(\vec{a} - \vec{n}) + \beta(\vec{b} - \vec{n}) + \gamma(\vec{c} - \vec{n}),$$

$$(\vec{y} - \vec{n}) = \alpha'(\vec{a} - \vec{n}) + \beta'(\vec{b} - \vec{n}) + \gamma'(\vec{c} - \vec{n}),$$

$$(\vec{z} - \vec{n}) = \alpha''(\vec{a} - \vec{n}) + \beta''(\vec{b} - \vec{n}) + \gamma''(\vec{c} - \vec{n}).$$

The above equations can be further changed into the matrix forms:

$$(\vec{x} - \vec{n}) = \begin{bmatrix} \vec{a} - \vec{n} & \vec{b} - \vec{n} & \vec{c} - \vec{n} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \\ \gamma \end{bmatrix},$$

$$(\vec{y} - \vec{n}) = \begin{bmatrix} \vec{a} - \vec{n} & \vec{b} - \vec{n} & \vec{c} - \vec{n} \end{bmatrix} \begin{bmatrix} \alpha' \\ \beta' \\ \gamma' \end{bmatrix},$$

and

$$(\vec{z} - \vec{n}) = \begin{bmatrix} \vec{a} - \vec{n} & \vec{b} - \vec{n} & \vec{c} - \vec{n} \end{bmatrix} \begin{bmatrix} \alpha'' \\ \beta'' \\ \gamma'' \end{bmatrix}.$$

The method of linear regression provides the solutions for α , β , γ , α' , β' , γ' , α'' , β'' and γ'' :

$$\begin{bmatrix} \alpha \\ \beta \\ \gamma \end{bmatrix} = (X^T X)^{-1} X^T (\vec{x} - \vec{n}),$$

$$\begin{bmatrix} \alpha' \\ \beta' \\ \gamma' \end{bmatrix} = (X^T X)^{-1} X^T (\vec{y} - \vec{n}),$$

$$\begin{bmatrix} \alpha'' \\ \beta'' \\ \gamma'' \end{bmatrix} = (X^T X)^{-1} X^T (\vec{z} - \vec{n}),$$

where X is a (number of isotopes) \times 3 matrix, with columns $(\vec{a} - \vec{n})$, $(\vec{b} - \vec{n})$ and $(\vec{c} - \vec{n})$.

Now, determine the crossover proportions for each source. The total number of moles from each spike in each species at the time of measurement must satisfy:

$$\frac{(1 - q_{12} - q_{13})m_a}{r_{21}m_b} = \frac{\alpha}{\beta}, \quad \frac{q_{12}m_a}{(1 - r_{21} - r_{23})m_b} = \frac{\alpha'}{\beta'}, \quad \frac{q_{13}m_a}{r_{23}m_b} = \frac{\alpha''}{\beta''},$$

$$\frac{s_{31}m_c}{r_{21}m_b} = \frac{\gamma}{\beta}, \quad \frac{s_{32}m_c}{(1 - r_{21} - r_{23})m_b} = \frac{\gamma'}{\beta'}, \quad \frac{(1 - s_{31} - s_{32})m_c}{r_{23}m_b} = \frac{\gamma''}{\beta''},$$

$$\frac{(1 - q_{12} - q_{13})m_a}{s_{31}m_c} = \frac{\alpha}{\gamma}, \quad \frac{q_{13}m_a}{(1 - s_{31} - s_{32})m_c} = \frac{\alpha''}{\gamma''}.$$

These equations can be written in matrix form as following:

$$\begin{bmatrix} m_a\beta & m_a\beta & m_b\alpha & 0 & 0 & 0 \\ m_a\beta' & 0 & m_b\alpha' & m_b\alpha' & 0 & 0 \\ m_a\gamma & m_a\gamma & 0 & 0 & m_c\alpha & 0 \\ 0 & m_a\gamma'' & 0 & 0 & m_c\alpha'' & m_c\alpha'' \\ 0 & 0 & m_b\gamma' & m_b\gamma' & 0 & m_c\beta' \\ 0 & 0 & 0 & m_b\gamma'' & m_c\beta'' & m_c\beta'' \end{bmatrix} \begin{bmatrix} q_{12} \\ q_{13} \\ r_{21} \\ r_{23} \\ s_{31} \\ s_{32} \end{bmatrix} = \begin{bmatrix} m_a\beta \\ m_b\alpha' \\ m_a\gamma \\ m_c\alpha'' \\ m_b\gamma' \\ m_c\beta'' \end{bmatrix}.$$

Solving the above equations gives the estimates of q_{12} , q_{13} , r_{21} , r_{23} , s_{31} and s_{32} .

From (2.45) – (2.47), it is given that the ratio of the total number of moles of Cr(III) from the sample to the total number of moles from spike A at the time of measurement is equal to the ratio of $1 - \alpha - \beta - \gamma$ to α . Thus

$$\frac{1 - \alpha - \beta - \gamma}{\alpha} = \frac{[(1 - q_{12} - q_{13})p_1 + r_{21}p_2 + s_{31}(1 - p_1 - p_2)]m_n}{(1 - q_{12} - q_{13})m_a}. \quad (2.48)$$

Similarly,

$$\frac{1 - \alpha' - \beta' - \gamma'}{\beta'} = \frac{[q_{12}p_1 + (1 - r_{21} - r_{23})p_2 + s_{32}(1 - p_1 - p_2)]m_n}{(1 - r_{21} - r_{23})m_b}, \quad (2.49)$$

and

$$\frac{1 - \alpha'' - \beta'' - \gamma''}{\gamma''} = \frac{[q_{13}p_1 + r_{23}p_2 + (1 - s_{31} - s_{32})(1 - p_1 - p_2)]m_n}{(1 - s_{31} - s_{32})m_c}. \quad (2.50)$$

So the total number of moles originating in the natural sample is

$$\begin{aligned} m_n &= \frac{1 - \alpha - \beta - \gamma}{\alpha}(1 - q_{12} - q_{13})m_a + \frac{1 - \alpha' - \beta' - \gamma'}{\beta'}(1 - r_{21} - r_{23})m_b \\ &+ \frac{1 - \alpha'' - \beta'' - \gamma''}{\gamma''}(1 - s_{31} - s_{32})m_c. \end{aligned} \quad (2.51)$$

From (2.48),

$$(1 - q_{12} - q_{13})(1 - \alpha - \beta - \gamma)m_a - s_{31}\alpha m_n = (1 - q_{12} - q_{13} - s_{31})\alpha m_n p_1 + (r_{21} - s_{31})\alpha m_n p_2. \quad (2.52)$$

From (2.49),

$$(1 - r_{21} - r_{23})(1 - \alpha' - \beta' - \gamma')m_b - s_{32}\beta' m_n = (q_{12} - s_{32})\beta' m_n p_1 + (1 - r_{21} - r_{23} - s_{32})\beta' m_n p_2. \quad (2.53)$$

Simplify (2.52) and (2.53) to get the following two equations:

$$A_1 = B_1 p_1 + C_1 p_2$$

$$A_2 = B_2 p_1 + C_2 p_2,$$

where

- $A_1 = (1 - q_{12} - q_{13})(1 - \alpha - \beta - \gamma)m_a - s_{31}\alpha m_n$
- $B_1 = (1 - q_{12} - q_{13} - s_{31})\alpha m_n$
- $C_1 = (r_{21} - s_{31})\alpha m_n$
- $A_2 = (1 - r_{21} - r_{23})(1 - \alpha' - \beta' - \gamma')m_b - s_{32}\beta' m_n$
- $B_2 = (q_{12} - s_{32})\beta' m_n$
- $C_2 = (1 - r_{21} - r_{23} - s_{32})\beta' m_n.$

Solving for the unknowns p_1 and p_2 gives:

$$p_1 = \frac{A_2 C_1 - A_1 C_2}{B_2 C_1 - B_1 C_2}, \quad p_2 = \frac{A_1 B_2 - A_2 B_1}{B_2 C_1 - B_1 C_2}.$$

Then the concentration of Cr(III) in the original sample is equal to $p_1 c_n = p_1(m_n(\vec{n}^T \cdot \vec{w})) / (v_n \times (10^{-3} mL / \mu L))$; the concentration of Cr(VI) is equal to $p_2 c_n =$

$p_2(m_n(\vec{n}^T \cdot \vec{w}))/ (v_n \times (10^{-3}mL/\mu L))$; and the concentration of Cr(IX) is equal to $(1 - p_1 - p_2)c_n = (1 - p_1 - p_2)(m_n(\vec{n}^T \cdot \vec{w}))/ (v_n \times (10^{-3}mL/\mu L))$.

Although the matrix method presented here has never appeared in literature, Meija, et al 2006, proposed a related matrix solution method using a matrix form based on the isotope pattern deconvolution analysis in order to simplify the complexity of the calculations of the system of the four equations.

Consider the original sample, the spike and the mixture of the sample and the spike. Since the number of atoms of the mixture (N_m) equals the sum of the number of atoms of the sample (N_a) plus the number of atoms of the spike (N_s), then

$$\begin{pmatrix} N_a^1 \\ N_a^2 \\ \dots \\ N_a^n \end{pmatrix} + \begin{pmatrix} N_s^1 \\ N_s^2 \\ \dots \\ N_s^n \end{pmatrix} = \begin{pmatrix} N_m^1 \\ N_m^2 \\ \dots \\ N_m^n \end{pmatrix}. \quad (2.54)$$

Rewrite it as the following:

$$N_a \cdot \begin{pmatrix} A_a^1 \\ A_a^2 \\ \dots \\ A_a^n \end{pmatrix} + N_s \cdot \begin{pmatrix} A_s^1 \\ A_s^2 \\ \dots \\ A_s^n \end{pmatrix} = N_m \cdot \begin{pmatrix} A_m^1 \\ A_m^2 \\ \dots \\ A_m^n \end{pmatrix} = (N_a + N_s)s \cdot \begin{pmatrix} I_m^1 \\ I_m^2 \\ \dots \\ I_m^n \end{pmatrix}, \quad (2.55)$$

where $(A_a^1, A_a^2, \dots, A_a^n)$ and $(A_s^1, A_s^2, \dots, A_s^n)$ are the isotopic compositions of the sample and the spike, respectively, and $(I_m^1, I_m^2, \dots, I_m^n)$ is the measured isotopic intensities of the mixture. Here s is the unknown instrumental sensitivity coefficient.

Dividing both sides of (2.55) by $(N_a + N_s)s$ yields:

$$\begin{pmatrix} I_m^1 \\ I_m^2 \\ \dots \\ I_m^n \end{pmatrix} = \begin{pmatrix} A_a^1 & A_s^1 \\ A_a^2 & A_s^2 \\ \dots & \dots \\ A_a^n & A_s^n \end{pmatrix} \cdot \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}, \quad (2.56)$$

where $b_1 = \frac{N_a}{N_a+N_s}s$, and $b_2 = \frac{N_s}{N_a+N_s}s$. Multiple regression method can be used on (2.56) to find the estimates of b_1 and b_2 . The following relationship can be obtained from these estimates:

$$\frac{b_1}{b_2} = \frac{N_a}{N_s} = \frac{n_a}{n_s}, \quad (2.57)$$

where n is number of moles.

For the specific case of two species and three isotopes, the matrix equations analogous to (2.56) are,

$$\begin{pmatrix} I_{Cr(III)} \\ \dots \\ I_{Cr(III)} \end{pmatrix} = \begin{pmatrix} A_{Cr(III)}^s & A_{Cr(VI)}^s & A_{Cr} \\ \dots & \dots & \dots \\ A_{Cr(III)}^s & A_{Cr(VI)}^s & A_{Cr} \end{pmatrix} \cdot \begin{pmatrix} a_1 \\ b_1 \\ c_1 \end{pmatrix}, \quad (2.58)$$

$$\begin{pmatrix} I_{Cr(VI)} \\ \dots \\ I_{Cr(VI)} \end{pmatrix} = \begin{pmatrix} A_{Cr(III)}^s & A_{Cr(VI)}^s & A_{Cr} \\ \dots & \dots & \dots \\ A_{Cr(III)}^s & A_{Cr(VI)}^s & A_{Cr} \end{pmatrix} \cdot \begin{pmatrix} a_2 \\ b_2 \\ c_2 \end{pmatrix}. \quad (2.59)$$

The two corresponding sets of parameters (a_1, b_1, c_1) and (a_2, b_2, c_2) can be found by using multiple regression. The estimates of the four unknowns can then be found using the Scheme 1 presented in [12].

2.4 Newton's Method

In many situations, Newton's method is a very efficient algorithm for finding the roots of real-valued functions. In particular, it can be applied to the system of equations (1.1)–(1.4), or (1.5)–(1.13). Consider the system of equations $\mathbf{f}(\mathbf{x}) = 0$, where $\mathbf{f} = (f_1, \dots, f_k)'$ and $\mathbf{x} = (x_1, \dots, x_k)'$. Starting from an arbitrary initial value $\mathbf{x}^{(0)}$, Newton's method takes iterations

$$\mathbf{x}^{(n)} = \mathbf{x}^{(n-1)} - J^{-1}(\mathbf{x}^{(n-1)})\mathbf{f}(\mathbf{x}^{(n-1)}), \quad n = 1, 2, \dots, \quad (2.60)$$

where

$$J = \begin{pmatrix} \frac{\partial f_1}{\partial x_1} & \dots & \frac{\partial f_1}{\partial x_k} \\ \vdots & \vdots & \vdots \\ \frac{\partial f_k}{\partial x_1} & \dots & \frac{\partial f_k}{\partial x_k} \end{pmatrix} \quad (2.61)$$

is the Jacobian matrix of \mathbf{f} . The iterations can be stopped when the change in the successive updates does not exceed a pre-specified tolerance. As long as the function \mathbf{f} is differentiable and the Jacobian matrix J is not singular in a neighborhood of the true solution, Newton's method is guaranteed to converge given that the starting point is chosen appropriately.

To apply Newton's method to the two species case, rewrite (1.1) – (1.4) as functions of x , y , α and β :

$$\begin{aligned} f_1 = (A_1 - A_2R_1)x - (A_1 - A_2R_1)x\alpha + (A_1 - A_2R_1)y\beta \\ - (B_1 - B_3R_1)\alpha + (B_2 - B_4R_1)\beta + B_1 - B_3R_1 = 0 \end{aligned} \quad (2.62)$$

$$\begin{aligned} f_2 = (A_3 - A_2R_2)x - (A_3 - A_2R_2)x\alpha + (A_3 - A_2R_2)y\beta \\ - (B_5 - B_3R_2)\alpha + (B_6 - B_4R_2)\beta + B_5 - B_3R_2 = 0 \end{aligned} \quad (2.63)$$

$$\begin{aligned}
f_3 = & (A_1 - A_2R_3)x\alpha + (A_1 - A_2R_3)y + (-A_1 + A_2R_3)y\beta \\
& + (B_1 - B_3R_3)\alpha + (-B_2 + B_4R_3)\beta + B_2 - B_4R_3 = 0 \quad (2.64)
\end{aligned}$$

$$\begin{aligned}
f_4 = & (A_3 - A_2R_4)x\alpha + (A_3 - A_2R_4)y + (-A_3 + A_2R_4)y\beta \\
& + (B_5 - B_3R_4)\alpha + (-B_6 + B_4R_4)\beta + B_6 - B_4R_4 = 0, \quad (2.65)
\end{aligned}$$

where

- $R_1 = R_{50/52}^{III}$, $R_2 = R_{53/52}^{III}$, $R_3 = R_{50/52}^{VI}$, $R_4 = R_{53/52}^{VI}$
- $A_1 = {}^{50}A_x$, $A_2 = {}^{52}A_x$, $A_3 = {}^{53}A_x$
- $B_1 = {}^{50}A_s^{III}N_s^{III}$, $B_2 = {}^{50}A_s^{VI}N_s^{VI}$, $B_3 = {}^{52}A_s^{III}N_s^{III}$, $B_4 = {}^{52}A_s^{VI}N_s^{VI}$, $B_5 = {}^{53}A_s^{III}N_s^{III}$, $B_6 = {}^{53}A_s^{VI}N_s^{VI}$
- $x = N_x^{III}$, $y = N_x^{VI}$.

Based on (2.62) – (2.65), the Jacobian matrix is

$$\begin{aligned}
J &= \begin{pmatrix} \partial f_1/\partial x & \partial f_1/\partial \beta & \partial f_1/\partial y & \partial f_1/\partial \alpha \\ \partial f_2/\partial x & \partial f_2/\partial \beta & \partial f_2/\partial y & \partial f_2/\partial \alpha \\ \partial f_3/\partial x & \partial f_3/\partial \beta & \partial f_3/\partial y & \partial f_3/\partial \alpha \\ \partial f_4/\partial x & \partial f_4/\partial \beta & \partial f_4/\partial y & \partial f_4/\partial \alpha \end{pmatrix} \\
&= \begin{pmatrix} P\Phi & Py + (B_2 - B_4R_1) & P\beta & -Px - (B_1 - B_3R_1) \\ Q\Phi & Qy + (B_6 - B_4R_2) & Q\beta & -Qx - (B_5 - B_3R_2) \\ R\alpha & -Ry + (-B_2 + B_4R_3) & R\Psi & Rx + (B_1 - B_3R_3) \\ S\alpha & -Sy + (-B_6 + B_4R_4) & S\Psi & Sx + (B_5 - B_3R_4) \end{pmatrix}, \quad (2.66)
\end{aligned}$$

where $P = A_1 - A_2R_1$, $Q = A_3 - A_2R_2$, $R = A_1 - A_2R_3$, $S = A_3 - A_2R_4$, $\Phi = 1 - \alpha$, $\Psi = 1 - \beta$.

For the general case involving k species, the k^2 by k^2 Jacobian matrix is defined similarly. See Appendix B for the result of the three species Jacobian matrix.

Chapter 3

Solution Methods and Analysis

For the case involving two species and a system of four equations, it is easy to find the deterministic solution by using MAPLE software. However, for the cases involving three or more species, it is too time consuming if possible at all to get the deterministic solution from MAPLE or other software. As a result, iterative methods, such as Newton's method, can be implemented to find the solution in these cases.

The iterative method introduced in Section 2.2 can be explained by using Fixed Point of nonlinear equations. Let f_1, \dots, f_4 be defined as in (2.62) – (2.65). Since $f_1 = 0$ and $f_2 = 0$ have explicit solutions for x and β when given y and α , and $f_3 = 0$ and $f_4 = 0$ have explicit solutions for y and α when given x and β , we can rewrite $f_1 = 0, \dots, f_4 = 0$ as

$$\begin{pmatrix} x \\ \beta \\ y \\ \alpha \end{pmatrix} = \begin{pmatrix} g_1(y, \alpha) \\ g_2(y, \alpha) \\ g_3(x, \beta) \\ g_4(x, \beta) \end{pmatrix}, \quad (3.1)$$

where

$$g_1(y, \alpha) = \frac{B_2 C_1 - B_1 C_2}{A_1 B_2 - A_2 B_1}, \quad g_2(y, \alpha) = \frac{A_1 C_2 - A_2 C_1}{A_1 B_2 - A_2 B_1},$$
$$g_3(x, \beta) = \frac{B_4 C_3 - B_3 C_4}{A_3 B_4 - A_4 B_3}, \quad g_4(x, \beta) = \frac{A_3 C_4 - A_4 C_3}{A_3 B_4 - A_4 B_3}$$

as given in (2.5) and (2.10). Iterations can be defined using (3.1). Given starting values, updated values can be obtained using the g functions on the right-hand side of (3.1). From the theory [11] of the Fixed Point problem, if the above iteration converges, it must converge to a fixed point of (3.1), i.e., a solution to $f_1 = 0, \dots, f_4 = 0$. Furthermore, if the starting point is close enough to the solution and the following Conditions [11] are satisfied, then it is guaranteed that the iterations will converge to the solution.

Conditions. *For a two species problem, the fixed point method iterating using (3.1) is guaranteed to converge to the true values if*

$$\begin{aligned} & \left| \frac{\partial g_1(y, \alpha)}{\partial x} \right| + \left| \frac{\partial g_1(y, \alpha)}{\partial \beta} \right| + \left| \frac{\partial g_1(y, \alpha)}{\partial y} \right| + \left| \frac{\partial g_1(y, \alpha)}{\partial \alpha} \right| < 1, \\ & \left| \frac{\partial g_2(y, \alpha)}{\partial x} \right| + \left| \frac{\partial g_2(y, \alpha)}{\partial \beta} \right| + \left| \frac{\partial g_2(y, \alpha)}{\partial y} \right| + \left| \frac{\partial g_2(y, \alpha)}{\partial \alpha} \right| < 1, \\ & \left| \frac{\partial g_3(x, \beta)}{\partial x} \right| + \left| \frac{\partial g_3(x, \beta)}{\partial \beta} \right| + \left| \frac{\partial g_3(x, \beta)}{\partial y} \right| + \left| \frac{\partial g_3(x, \beta)}{\partial \alpha} \right| < 1, \\ & \left| \frac{\partial g_4(x, \beta)}{\partial x} \right| + \left| \frac{\partial g_4(x, \beta)}{\partial \beta} \right| + \left| \frac{\partial g_4(x, \beta)}{\partial y} \right| + \left| \frac{\partial g_4(x, \beta)}{\partial \alpha} \right| < 1, \end{aligned}$$

given that the starting point is close enough to the true values.

The iterative method introduced in Section 2.2 is actually a special case of Fixed Point Iteration which proposes to use the updated values of x and β from g_1 and g_2 in the updating of y and α using g_3 and g_4 .

It is not hard to show that the following four partial derivatives in Conditions are all constants with respect to x , y , α and β :

$$\begin{aligned} \frac{\partial g_1}{\partial y} = & (R_{50/52}^{III} ({}^{53}A_x {}^{52}A_s^{III} - {}^{52}A_x {}^{53}A_s^{III}) N_s^{III} + R_{53/52}^{III} ({}^{52}A_x {}^{50}A_s^{III} - {}^{50}A_x {}^{52}A_s^{III}) N_s^{III} \\ & + ({}^{50}A_x {}^{53}A_s^{III} - {}^{53}A_x {}^{50}A_s^{III}) N_s^{III}) / (R_{50/52}^{III} ({}^{53}A_x {}^{52}A_s^{VI} - {}^{52}A_x {}^{53}A_s^{VI}) N_s^{VI} \\ & + R_{53/52}^{III} ({}^{52}A_x {}^{50}A_s^{VI} - {}^{50}A_x {}^{52}A_s^{VI}) N_s^{VI} + ({}^{50}A_x {}^{53}A_s^{VI} - {}^{53}A_x {}^{50}A_s^{VI}) N_s^{VI}); \end{aligned}$$

$$\begin{aligned}
\frac{\partial g_2}{\partial \alpha} &= (-R_{50/52}^{III}(^{52}A_x \ ^{53}A_s^{III} - ^{53}A_x \ ^{52}A_s^{III})N_s^{III} - R_{53/52}^{III}(^{50}A_x \ ^{52}A_s^{III} - ^{52}A_x \ ^{50}A_s^{III})N_s^{III} \\
&\quad - (^{53}A_x \ ^{50}A_s^{III} - ^{50}A_x \ ^{53}A_s^{III})N_s^{III}) / (R_{50/52}^{III}(^{53}A_x \ ^{52}A_s^{VI} - ^{52}A_x \ ^{53}A_s^{VI})N_s^{VI} \\
&\quad + R_{53/52}^{III}(^{52}A_x \ ^{50}A_s^{VI} - ^{50}A_x \ ^{52}A_s^{VI})N_s^{VI} + (^{50}A_x \ ^{53}A_s^{VI} - ^{53}A_x \ ^{50}A_s^{VI})N_s^{VI}); \\
\frac{\partial g_3}{\partial x} &= (R_{50/52}^{VI}(^{53}A_x \ ^{52}A_s^{VI} - ^{52}A_x \ ^{53}A_s^{VI})N_s^{VI} + R_{53/52}^{VI}(^{52}A_x \ ^{50}A_s^{VI} - ^{50}A_x \ ^{52}A_s^{VI})N_s^{VI} \\
&\quad + (^{50}A_x \ ^{53}A_s^{VI} - ^{53}A_x \ ^{50}A_s^{VI})N_s^{VI}) / (R_{50/52}^{VI}(^{53}A_x \ ^{52}A_s^{III} - ^{52}A_x \ ^{53}A_s^{III})N_s^{III} \\
&\quad + R_{53/52}^{VI}(^{52}A_x \ ^{50}A_s^{III} - ^{50}A_x \ ^{52}A_s^{III})N_s^{III} + (^{50}A_x \ ^{53}A_s^{III} - ^{53}A_x \ ^{50}A_s^{III})N_s^{III}); \\
\frac{\partial g_4}{\partial \beta} &= (-R_{50/52}^{VI}(^{52}A_x \ ^{53}A_s^{VI} - ^{53}A_x \ ^{52}A_s^{VI})N_s^{VI} - R_{53/52}^{VI}(^{50}A_x \ ^{52}A_s^{VI} - ^{52}A_x \ ^{50}A_s^{VI})N_s^{VI} \\
&\quad - (^{53}A_x \ ^{50}A_s^{VI} - ^{50}A_x \ ^{53}A_s^{VI})N_s^{VI}) / (R_{50/52}^{VI}(^{53}A_x \ ^{52}A_s^{III} - ^{52}A_x \ ^{53}A_s^{III})N_s^{III} \\
&\quad + R_{53/52}^{VI}(^{52}A_x \ ^{50}A_s^{III} - ^{50}A_x \ ^{52}A_s^{III})N_s^{III} + (^{50}A_x \ ^{53}A_s^{III} - ^{53}A_x \ ^{50}A_s^{III})N_s^{III}).
\end{aligned}$$

The twelve remaining partial derivatives are all zero: $\partial g_1/\partial x = \partial g_1/\partial \beta = \partial g_1/\partial \alpha = \partial g_2/\partial x = \partial g_2/\partial \beta = \partial g_2/\partial y = \partial g_3/\partial \beta = \partial g_3/\partial y = \partial g_3/\partial \alpha = \partial g_4/\partial x = \partial g_4/\partial y = \partial g_4/\partial \alpha = 0$.

It is difficult to verify the **Conditions** analytically due to the large number of parameters involved. Instead, the **Conditions** are numerically verified in the simulations provided later in this chapter. Note that the code used to check these **Conditions** for the simulations can also be used prior to implementing the iterative method in real applications.

Newton's method is generally better than the iterative method in terms of convergence speed. In the simulations provided later in this chapter, Newton's method always converges within three steps. The number of steps required for the iterative method to converge, however, varies from one to more than sixty. (It converges faster if some unknowns are zero.) The observed improved convergence speed of Newton's method over the iterative method does not come without cost. Newton's method requires calculation of the Jacobian matrix and its inverse but the iterative method does not. Both methods estimate the unknowns very accurately.

The matrix method is derived from a different point of view than the deterministic method, yet yields solutions identical to those from the deterministic method. In the deterministic method, there are four unknowns: C_x^{III}, C_x^{VI} (the concentrations of chromium III and VI), α and β (crossover parameters). In the matrix method, the four unknowns are C_n (the unknown sample concentration of chromium), p (the proportion of the chromium in the sample that is in species Cr(III)), q and r (crossover parameters). There are four measurements in the deterministic method R_1, R_2, R_3 and R_4 . For the matrix method, the measurements are $(\frac{R_1}{R_1+1+R_2}, \frac{1}{R_1+1+R_2}, \frac{R_2}{R_1+1+R_2})$ and $(\frac{R_3}{R_3+1+R_4}, \frac{1}{R_3+1+R_4}, \frac{R_4}{R_3+1+R_4})$. The relationship among other parameters is $\mathbf{n} = ({}^{50}A_x, {}^{52}A_x, {}^{53}A_x)$, $\mathbf{a} = ({}^{50}A_s^{III}, {}^{52}A_s^{III}, {}^{53}A_s^{III})$, $\mathbf{b} = ({}^{50}A_s^{VI}, {}^{52}A_s^{VI}, {}^{53}A_s^{VI})$, $v_a \times 10^{-3} = W_s^{III}$, $v_b \times 10^{-3} = W_s^{VI}$, $v_n \times 10^{-3} = W_x$. This gives the following four equations that relate the unknowns of the matrix method to those of the deterministic or iterative methods.

$$c_n = \frac{W_x(C_x^{III} + C_x^{VI})(\mathbf{n}^T \cdot \boldsymbol{\omega})}{v_n}, \quad p = \frac{W_x C_x^{III}(\mathbf{n}^T \cdot \boldsymbol{\omega})}{c_n v_n}, \quad q = \alpha, \quad r = \beta. \quad (3.2)$$

We provide simulations to examine the properties of these four solution methods. For the deterministic method, the iterative method and Newton's method, we use the same parameter values. We set ${}^{50}A_x = 0.04455$, ${}^{52}A_x = 0.85815$, ${}^{53}A_x = 0.0973$, ${}^{50}A_s^{III} = 0.0003$, ${}^{52}A_s^{III} = 0.0219$, ${}^{53}A_s^{III} = 0.9778$, ${}^{50}A_s^{VI} = 0.931$, ${}^{52}A_s^{VI} = 0.068$, ${}^{53}A_s^{VI} = 0.001$, $C_s^{III} = C_s^{VI} = 100(\mu\text{mole}/g)$, $W_s^{III} = W_s^{VI} = 25(g)$, and $W_x = 100(g)$. In order to be comparable to the other three methods, we set the parameters of the matrix method according to (3.2) as shown in the second column of Table 3.2.

Eight different combinations of values of $C_x^{III}, C_x^{VI}, \alpha$ and β are tested as shown in the second column of Table 3.3. It is assumed that these are the true parameter values. Before implementing any of our solution methods, the true values are used

to calculate the ratios $R_{50/52}^{III}$, $R_{53/52}^{III}$, $R_{50/52}^{VI}$ and $R_{53/52}^{VI}$. Then the ratios are used in combination with other known parameter values to implement all solution methods. In our simulations, the iterative method and Newton's method are started from the same values, that is, $C_x^{III} = C_x^{VI} = \alpha = \beta = 0$. However, based on further numerical experiments, we found that Newton's method and the iterative method work for a variety of starting values, including negative concentrations and/or crossover proportions. However, there exist initial conditions that do not yield convergence. This occurs when setting $\alpha = 1$ and $\beta = 0$ (or $\alpha = 0$ and $\beta = 1$) in Newton's method, or, when setting $\alpha = 1$ in the iterative method. The simulation results are shown in Table 3.3.

Table 3.3 indicates that the results obtained from the deterministic method, the iterative method, Newton's method and the matrix method are exactly the same as the true values. Also the iterative method and Newton's method were always able to find the correct solution for all cases when we start from initial values $C_x^{III} = C_x^{VI} = \alpha = \beta = 0$.

Similarly, Table 3.4 consists of four different combinations of values of nine unknowns for three species. The deterministic method is not considered because MAPLE was unable to solve the system of nine equations in reasonable time (if at all). Table 3.4 shows that the solutions from each of three methods are in perfect agreement with the true values.

Finally, the simulations are conducted to verify the sufficient conditions of the fixed point iteration which will guarantee the convergence. The results given in Table 3.1 using all eight different combinations of true values in Table 3.3 show that **Conditions** are satisfied for the two species case. (All **Conditions** are also satisfied for the three species case.)

(x, β, y, α)	$\frac{\partial g_1}{\partial y}$	$\frac{\partial g_2}{\partial \alpha}$	$\frac{\partial g_3}{\partial x}$	$\frac{\partial g_4}{\partial \beta}$
(100,0.5,100,0.2)	-0.625	-0.625	-0.4	-0.4
(100,0.5,1,0.2)	-0.625	-0.625	-0.4	-0.4
(100,0.1,30,0.6)	-0.25	-0.25	-0.667	-0.667
(100,0.5,30,0)	-0.5	-0.5	0	0
(100,0,100,0.7)	0	0	-0.7	-0.7
(100,0,30,0)	0	0	0	0
(0,0.5,30,0.2)	-0.625	-0.625	-0.4	-0.4
(100,0,0,0)	0	0	0	0

Table 3.1: Simulation results for iterative method convergence conditions

Deterministic method	Matrix method
R_1, R_2, R_3, R_4	$\left(\frac{R_1}{R_1+1+R_2}, \frac{1}{R_1+1+R_2}, \frac{R_2}{R_1+1+R_2}\right)$ $\left(\frac{R_3}{R_3+1+R_4}, \frac{1}{R_3+1+R_4}, \frac{R_4}{R_3+1+R_4}\right)$
${}^{50}A_x = 0.04455, {}^{52}A_x = 0.85815, {}^{53}A_x = 0.0973$	$\mathbf{n} = (0.04455, 0.85815, 0.0973)$
${}^{50}A_s^{III} = 0.0003, {}^{52}A_s^{III} = 0.0219, {}^{53}A_s^{III} = 0.9778$	$\mathbf{a} = (0.0003, 0.0219, 0.9778)$
${}^{50}A_s^{VI} = 0.931, {}^{52}A_s^{VI} = 0.068, {}^{53}A_s^{VI} = 0.001$	$\mathbf{b} = (0.931, 0.068, 0.001)$
$C_s^{III} = 100$ ($\mu\text{mole/g}$)	$c_a = 100$ (mg/mL)
$C_s^{VI} = 100$ ($\mu\text{mole/g}$)	$c_b = 100$ (mg/mL)
$W_s^{III} = 25$ (g)	$v_a = 25$ (μL)
$W_s^{VI} = 25$ (g)	$v_b = 25$ (μL)
$W_x = 100$ (g)	$v_n = 100$ (μL)
	$\omega = (49.9461, 51.9405, 52.9407)$

Table 3.2: Comparison of the required components for the deterministic method and matrix method

Unknowns	True values	Deterministic method	Iterative method	Newton's method	Matrix method
C_x^{III}	100	100	100	100	100
C_x^{VI}	100	100	100	100	100
α	0.2	0.2	0.2	0.2	0.2
β	0.5	0.5	0.5	0.5	0.5
C_x^{III}	100	100	100	100	100
C_x^{VI}	1	1	1	1	1
α	0.2	0.2	0.2	0.2	0.2
β	0.5	0.5	0.5	0.5	0.5
C_x^{III}	100	100	100	100	100
C_x^{VI}	30	30	30	30	30
α	0.6	0.6	0.6	0.6	0.6
β	0.1	0.1	0.1	0.1	0.1
C_x^{III}	100	100	100	100	100
C_x^{VI}	30	30	30	30	30
α	0	-1.05×10^{-17}	-3.5×10^{-18}	5.3×10^{-17}	-7.6×10^{-17}
β	0.5	0.5	0.5	0.5	0.5
C_x^{III}	100	100	100	100	100
C_x^{VI}	30	30	30	30	30
α	0.7	0.7	0.7	0.7	0.7
β	0	1.28×10^{-17}	2.2×10^{-18}	-1.5×10^{-17}	1.05×10^{-17}
C_x^{III}	100	100	100	100	100
C_x^{VI}	30	30	30	30	30
α	0	-5.8×10^{-18}	-7×10^{-18}	-1.14×10^{-17}	-1.5×10^{-16}
β	0	7×10^{-18}	7.3×10^{-18}	3.27×10^{-17}	3.5×10^{-17}
C_x^{III}	0	-5.96×10^{-15}	2.7×10^{-13}	7.5×10^{-15}	0
C_x^{VI}	30	30	30	30	30
α	0.2	0.2	0.2	0.2	0.2
β	0.5	0.5	0.5	0.5	0.5
C_x^{III}	100	100	100	100	100
C_x^{VI}	0	0	0	3.7×10^{-16}	0
α	0	0	0	1.96×10^{-18}	0
β	0	7×10^{-18}	7.3×10^{-18}	1.95×10^{-17}	3.5×10^{-17}

Table 3.3: Comparison of four solution methods (two species) for eight different sets of true values.

Unknowns	True values	Iterative method	Newton's method	Matrix method
C_x^{III}	100	100	100	100
C_x^{VI}	90	90	90	90
C_x^{IX}	50	50	50	50
α	0.2	0.2	0.2	0.2
β	0.3	0.3	0.3	0.3
γ	0.3	0.3	0.3	0.3
α'	0.3	0.3	0.3	0.3
β'	0.1	0.1	0.1	0.1
γ'	0.4	0.4	0.4	0.4
C_x^{III}	1000	1000	1000	1000
C_x^{VI}	900	900	900	900
C_x^{IX}	500	500	500	500
α	0.5	0.5	0.5	0.5
β	0.1	0.1	0.1	0.1
γ	0.2	0.2	0.2	0.2
α'	0.3	0.3	0.3	0.3
β'	0.2	0.2	0.2	0.2
γ'	0.1	0.1	0.1	0.1
C_x^{III}	50	50	50	50
C_x^{VI}	60	60	60	60
C_x^{IX}	10	10	10	10
α	0.1	0.1	0.1	0.1
β	0.2	0.2	0.2	0.2
γ	0.4	0.4	0.4	0.4
α'	0.05	0.05	0.05	0.05
β'	0.01	0.01	0.01	0.01
γ'	0.04	0.04	0.04	0.04
C_x^{III}	25	25	25	25
C_x^{VI}	75	75	75	75
C_x^{IX}	100	100	100	100
α	0	-7.3×10^{-18}	7.15×10^{-19}	4.29×10^{-17}
β	0.2	0.2	0.2	0.2
γ	0.4	0.4	0.4	0.4
α'	0.05	0.05	0.05	0.05
β'	0.01	0.01	0.01	0.01
γ'	0	3.9×10^{-18}	3.9×10^{-18}	-7.13×10^{-17}

Table 3.4: Comparison of three solution methods (three species) for four different sets of true values.

Chapter 4

Simulation Analysis

In order to determine the precision of the estimates of C_x^{III} , C_x^{VI} , α and β in the presence of uncertainty in the measurements $R_{50/52}^{III}$, $R_{53/52}^{III}$, $R_{50/52}^{VI}$ and $R_{53/52}^{VI}$, simulations are conducted for the case of two species. The deterministic solution method described in Chapter 3 is implemented using the true values $C_x^{III} = 100$, $C_x^{VI} = 30$, $\alpha = 0.6$ and $\beta = 0.1$. The uncertainty in the measurements is represented by simulating the mass spectrometer isotope ratio measurements according to

$$\tilde{R}_{50/52}^{III} \sim N(R_{50/52}^{III}, (\sigma \cdot R_{50/52}^{III})^2), \quad (4.1)$$

$$\tilde{R}_{53/52}^{III} \sim N(R_{53/52}^{III}, (\sigma \cdot R_{53/52}^{III})^2), \quad (4.2)$$

$$\tilde{R}_{50/52}^{VI} \sim N(R_{50/52}^{VI}, (\sigma \cdot R_{50/52}^{VI})^2), \quad (4.3)$$

$$\tilde{R}_{53/52}^{VI} \sim N(R_{53/52}^{VI}, (\sigma \cdot R_{53/52}^{VI})^2), \quad (4.4)$$

for three different values of σ . Note that \tilde{R} represents the mass spectrometer measurement, and R represents the true ratio. In order to get the sampling distribution of the estimates, 2500 simulations are conducted for each the three values of σ . The simulation results are summarized in Figures 4.1 – 4.5.

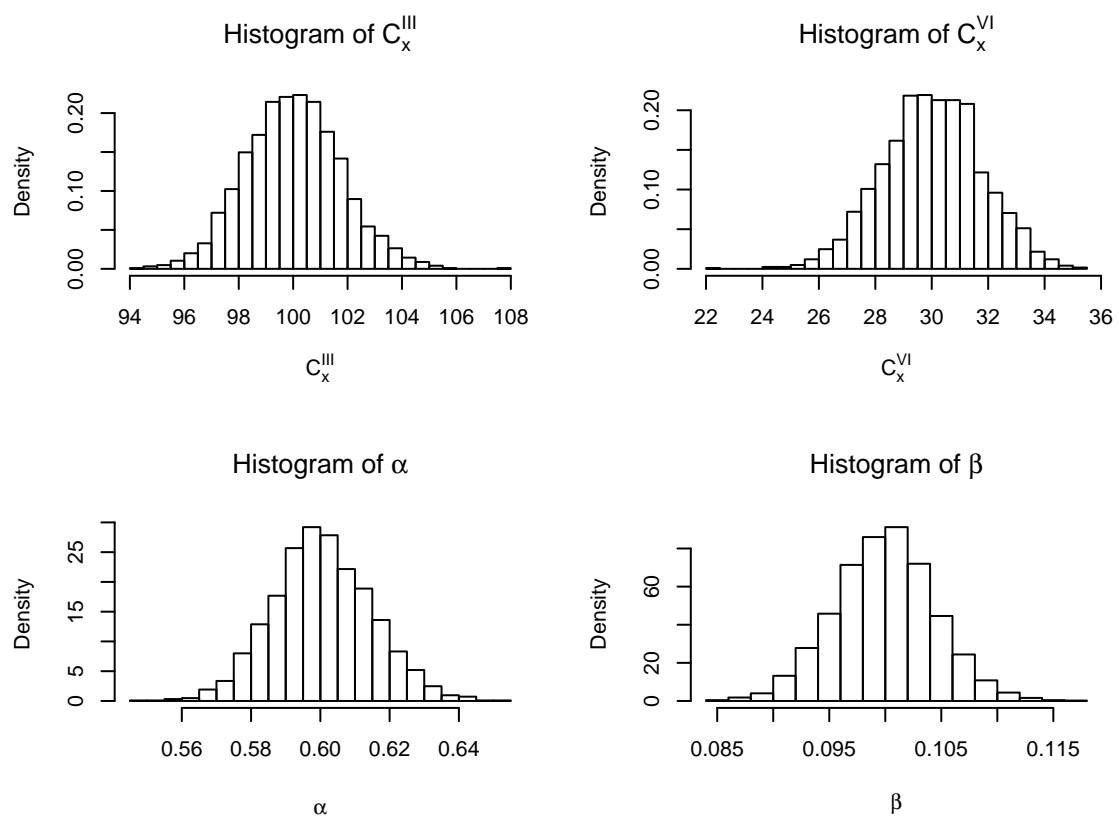


Figure 4.1: Sampling distributions of the estimates C_x^{III} , C_x^{VI} , α and β assuming the mass spectrometer standard deviation is $\sigma = 0.01$ of the true ratio.

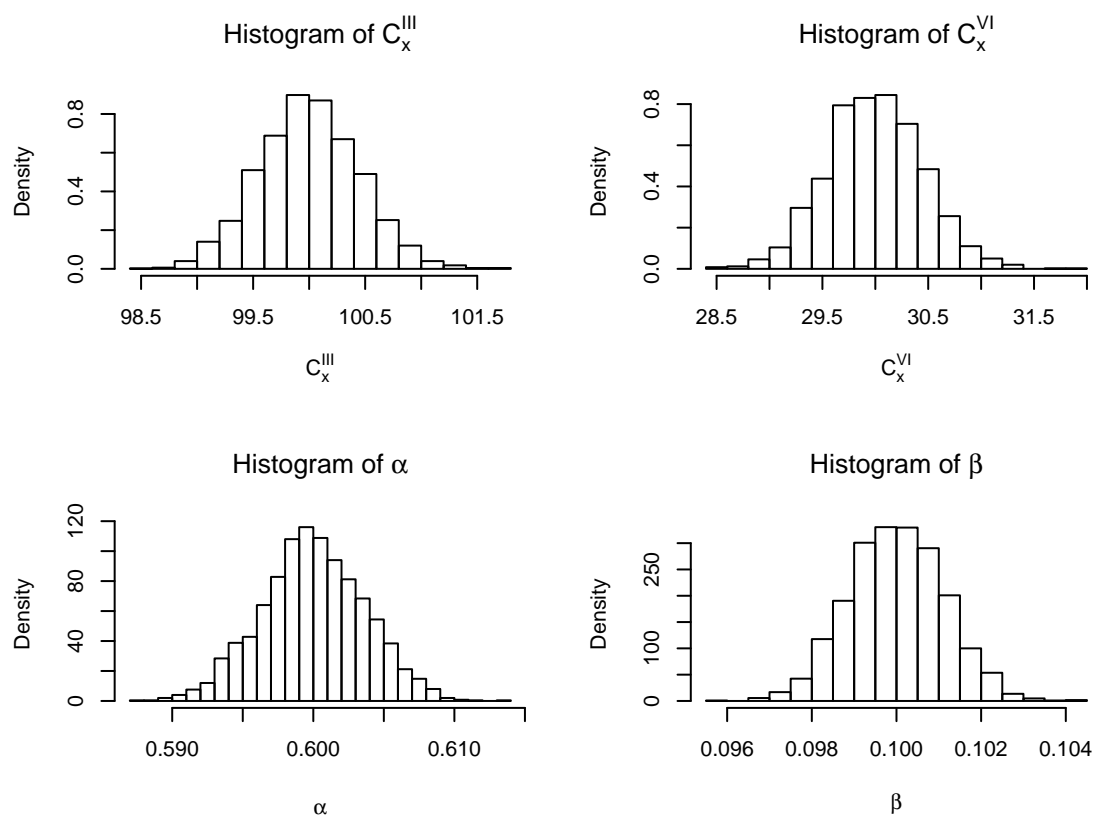


Figure 4.2: Sampling distributions of the estimates C_x^{III} , C_x^{VI} , α and β assuming the mass spectrometer standard deviation is $\sigma = 0.0025$ of the true ratio.

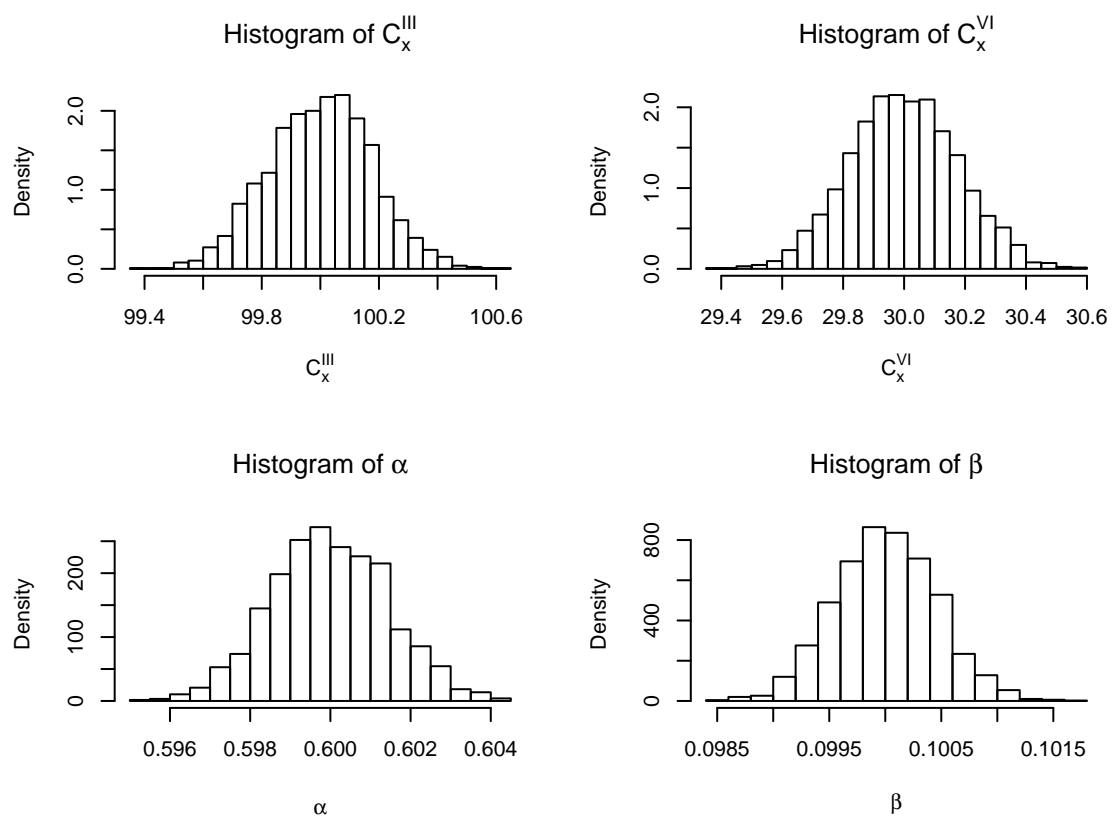


Figure 4.3: Sampling distributions of the estimates C_x^{III} , C_x^{VI} , α and β assuming the mass spectrometer standard deviation is $\sigma = 0.001$ of the true ratio.

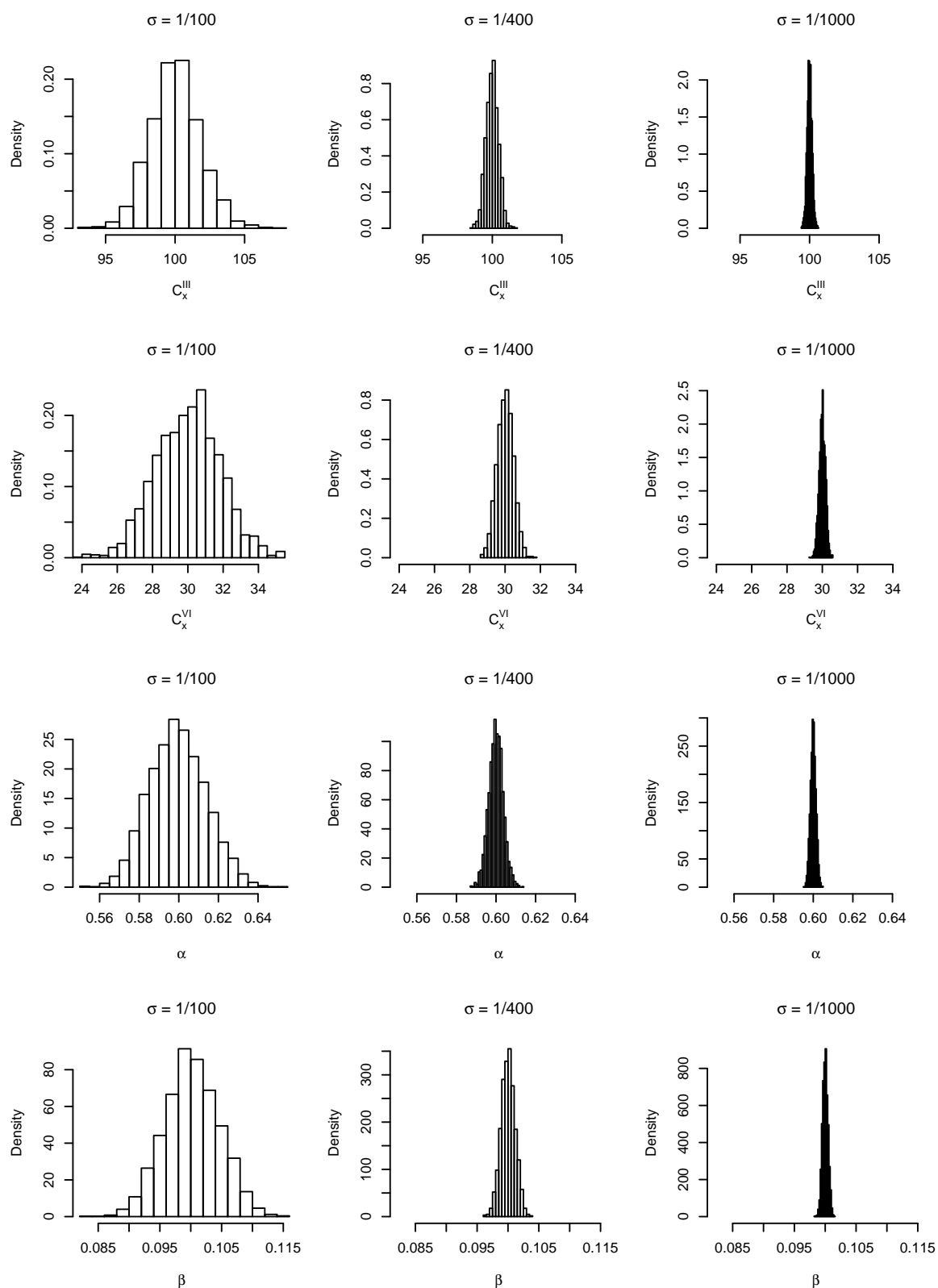


Figure 4.4: Sampling distributions of, respectively, C_x^{III} , C_x^{VI} , α , and β under three different mass spectrometer standard deviation multipliers: $\sigma = 1/100$; $\sigma = 1/400$; $\sigma = 1/1000$. The true values of C_x^{III} , C_x^{VI} , α , and β are 100, 30, 0.6, and 0.1, respectively.

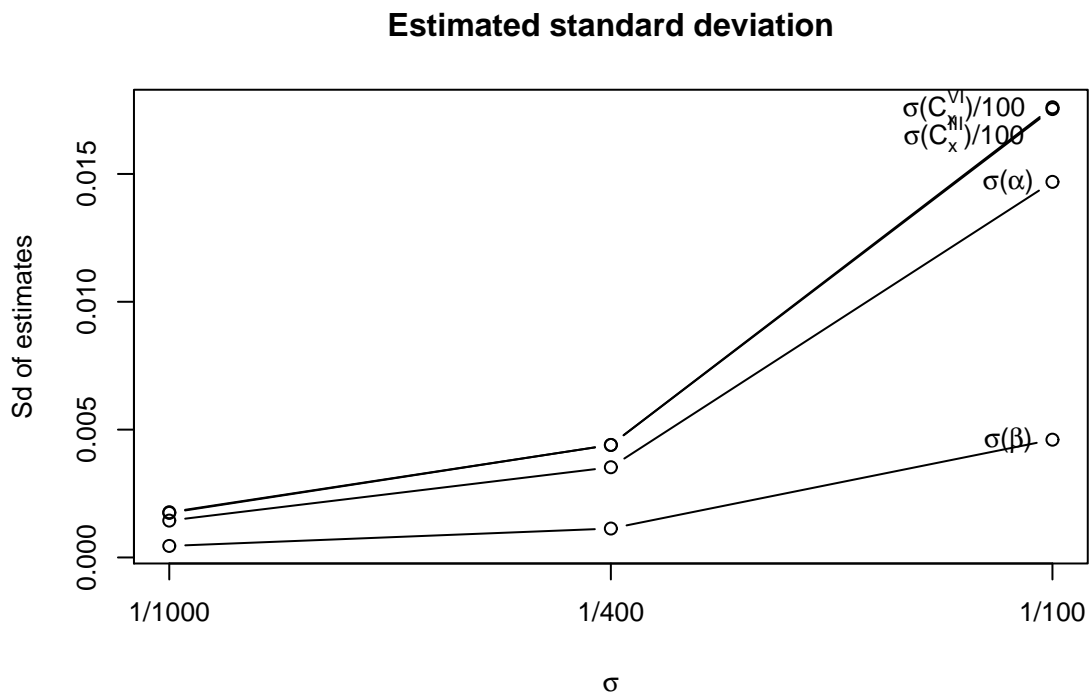


Figure 4.5: The standard deviation of the C_x^{III} , C_x^{VI} , α and β estimates as a function of the mass spectrometer standard deviation multiplier σ .

Chapter 5

Discussion

In this paper, the iterative method and the matrix method for solving SIDMS equations were reviewed. Also two new solution methods: the deterministic method and Newton's method were introduced. In Chapter 3, simulation studies show that all of these four solution methods estimate the unknowns accurately. These studies also suggest that the convergence speed of Newton's method is slightly faster than the iterative method. Note that these two methods always started with initial values of zero for all unknowns. Since it is possible to choose initial values that do not provide convergence (see Chapter 3), we recommend exclusive use of the deterministic method in the two species case.

The two-species case allows for easy estimation (due to availability of the deterministic method) of the uncertainty in the solutions using simulation analysis. In real applications where the means of (4.1) – (4.4) are not available, using the actual mass spectrometer measurements as the means will allow for estimation of the uncertainty in C_x^{III} , C_x^{VI} , α and β measurements.

In Chapter 4, simulations were conducted where it is assumed that the with-error mass spectrometer measurements $\tilde{R}_{50/52}^{III}$, $\tilde{R}_{53/52}^{III}$, $\tilde{R}_{50/52}^{VI}$, and $\tilde{R}_{53/52}^{VI}$ follow normal distributions. Replacing this normality assumption with a distributional assumption

deemed more appropriate does not change the manner in which the concentration and crossover proportion precisions are calculated. Simulation analysis to obtain the concentration and crossover proportion precisions for three species will require matrix inversions, and/or waiting for convergence, as the matrix method, Newton's method, or the iterative method must be used.

For the cases of $k = 4$ species or more, the deterministic method is unavailable because it is too time-consuming – if possible at all – to solve the system of k^2 equations by MAPLE or other software. The matrix method is currently also unavailable due to the complexity of the problem. However, we can use the iterative and Newton's methods to solve the k species cases. Recall, however, that Newton's method involves the calculation and inversion of the Jacobian matrix, which is large for $k \geq 4$, and it is not clear how these requirements will impact the convergence speed relative to the iterative method.

Appendix A

The deterministic solution of the system of four equations

First, simplify (1.1)-(1.4). Letting

- $R_1 = R_{50/52}^{III}, R_2 = R_{53/52}^{III}, R_3 = R_{50/52}^{VI}, R_4 = R_{53/52}^{VI}$
- $A_1 = {}^{50}A_x, A_2 = {}^{52}A_x, A_3 = {}^{53}A_x$
- $B_1 = {}^{50}A_s^{III}N_s^{III}, B_2 = {}^{50}A_s^{VI}N_s^{VI}, B_3 = {}^{52}A_s^{III}N_s^{III}, B_4 = {}^{52}A_s^{VI}N_s^{VI}, B_5 = {}^{53}A_s^{III}N_s^{III}, B_6 = {}^{53}A_s^{VI}N_s^{VI}$
- $x = N_x^{III}, y = N_x^{VI}$

yields the following equations:

$$R_1 = \frac{(A_1x + B_1)(1 - \alpha) + (A_1y + B_2)\beta}{(A_2x + B_3)(1 - \alpha) + (A_2y + B_4)\beta} \quad (\text{A.1})$$

$$R_2 = \frac{(A_3x + B_5)(1 - \alpha) + (A_3y + B_6)\beta}{(A_2x + B_3)(1 - \alpha) + (A_2y + B_4)\beta} \quad (\text{A.2})$$

$$R_3 = \frac{(A_1x + B_1)\alpha + (A_1y + B_2)(1 - \beta)}{(A_2x + B_3)\alpha + (A_2y + B_4)(1 - \beta)} \quad (\text{A.3})$$

$$R_4 = \frac{(A_3x + B_5)\alpha + (A_3y + B_6)(1 - \beta)}{(A_2x + B_3)\alpha + (A_2y + B_4)(1 - \beta)}. \quad (\text{A.4})$$

The deterministic solution to (2.1) – (2.4) is

$$x = \frac{-(R_3R_2B_3 - R_3B_5 - R_1R_4B_3 + R_1B_5 - R_2B_1 + R_4B_1)}{-R_3A_3 + R_3R_2A_2 + R_1A_3 + A_1R_4 - R_1A_2R_4 - R_2A_1} \quad (\text{A.5})$$

$$y = \frac{-(R_3R_2B_4 - R_3B_6 - R_1B_4R_4 + B_2R_4 - R_2B_2 + R_1B_6)}{-R_3A_3 + R_3R_2A_2 + R_1A_3 + A_1R_4 - R_1A_2R_4 - R_2A_1} \quad (\text{A.6})$$

$$\begin{aligned}
\alpha = & -(B_1 A_3^2 B_2 + B_6 A_1^2 B_5 + A_1^2 B_6^2 - R_4 B_4 A_1^2 B_5 - R_1 B_3 A_3^2 B_2 - B_1 A_3^2 R_3 B_4 \\
& - A_3 B_6 B_1 A_1 - R_2 B_3 A_1^2 B_6 - R_2 A_2 B_2^2 A_3 - A_1 B_6^2 R_3 A_2 - A_1^2 B_6 R_4 B_4 \\
& + R_1 A_2^2 B_6^2 R_3 - R_1 A_2 B_6^2 A_1 - B_2 A_3^2 R_3 B_4 - R_1 B_4 A_3^2 B_2 + R_1 B_4^2 A_3^2 R_3 \\
& + R_2 A_2^2 B_2^2 R_4 - R_2 B_4 A_1^2 B_6 + R_2 B_4^2 A_1^2 R_4 - 2A_1 B_6 B_2 A_3 - R_2 A_2^2 B_6 B_1 R_3 \\
& + R_2 A_2 B_6 B_1 A_1 + R_2 A_3 B_3 B_2 A_1 + R_2 B_3 A_1 B_6 R_3 A_2 + R_2 A_2^2 R_4 B_1 B_2 \\
& + R_2 B_3 A_1^2 R_4 B_4 + R_2 A_3 A_2 B_1 R_3 B_4 - R_2 A_2 A_1 R_4 B_3 B_2 - R_2 A_3 A_2 B_1 B_2 \\
& - R_2 A_2 R_4 B_4 B_1 A_1 + R_1 B_3 A_3^2 R_3 B_4 + R_1 B_3 A_3 B_2 R_4 A_2 + R_1 B_3 A_3 A_1 B_6 \\
& - R_1 B_3 A_3 A_1 R_4 B_4 - A_1 B_5 B_2 A_3 - B_1 R_4 A_2 B_2 A_3 + A_3 R_4 B_4 B_1 A_1 \\
& - B_6 A_1 B_5 R_3 A_2 + R_1 A_2 B_5 A_1 R_4 B_4 - R_2 A_3 B_3 R_3 B_4 A_1 - A_2 A_1 B_5 R_1 B_6 \\
& + A_2^2 R_3 B_5 R_1 B_6 - A_3 A_2 R_3 B_3 R_1 B_6 + B_1 A_3 R_3 A_2 B_6 + R_1 A_2 B_5 B_2 A_3 \\
& - R_1 A_2 B_5 R_3 B_4 A_3 - R_1 A_2^2 B_5 B_2 R_4 + A_1 B_5 R_3 B_4 A_3 + A_1 B_5 B_2 R_4 A_2 \\
& - R_2 A_2^2 R_3 B_6 B_2 + R_2 A_2 R_3 B_4 A_3 B_2 + R_2 A_3 B_4 B_2 A_1 + B_2^2 A_3^2 \\
& - R_2 A_3 B_4^2 R_3 A_1 + R_2 B_4 A_1 B_6 R_3 A_2 + A_1 B_6 R_3 B_4 A_3 + A_1 B_6 B_2 R_4 A_2 \\
& + R_1 A_2 B_6 A_1 R_4 B_4 + A_1 R_4 B_4 B_2 A_3 + R_1 A_2 R_4 B_4 B_2 A_3 + R_1 A_2 B_6 B_2 A_3 \\
& - R_1 A_2^2 B_6 B_2 R_4 - B_2^2 A_3 R_4 A_2 - R_1 B_4^2 A_3 A_1 R_4 + R_2 A_1 B_6 B_2 A_2 \\
& + R_1 B_4 A_3 A_1 B_6 + B_2 A_3 R_3 A_2 B_6 - 2R_2 A_2 R_4 B_4 B_2 A_1 - 2R_1 A_2 B_6 R_3 B_4 A_3) \\
& / (B_4 A_1 B_5 + A_3 B_3 B_2 - A_3 B_4 B_1 - A_2 B_5 B_2 + A_2 B_6 B_1 - B_3 A_1 B_6) \\
& (-R_3 A_3 + R_3 R_2 A_2 + R_1 A_3 + A_1 R_4 - R_1 A_2 R_4 - R_2 A_1) \tag{A.7}
\end{aligned}$$

$$\begin{aligned}
\beta = & (-B_1 A_3^2 B_2 - B_6 A_1^2 B_5 + A_1 B_5^2 R_1 A_2 - A_1^2 B_5^2 + A_1^2 B_5 R_2 B_3 + A_1^2 B_5 B_3 R_4 \\
& - B_1^2 R_4 A_2^2 R_2 + R_3 A_2 B_5^2 A_1 + A_3 B_1^2 R_2 A_2 + A_3 B_1^2 R_4 A_2 + A_3^2 B_1 R_1 B_3 \\
& - R_3 A_2^2 B_5^2 R_1 + R_4 B_4 A_1^2 B_5 - B_3^2 R_2 A_1^2 R_4 + R_1 B_3 A_3^2 B_2 + B_1 A_3^2 R_3 B_4 \\
& + R_3 A_3^2 B_3 B_1 - R_3 A_3^2 B_3^2 R_1 + A_3 B_6 B_1 A_1 + R_2 B_3 A_1^2 B_6 + 2A_3 A_1 B_5 B_1 \\
& - A_2 B_5 R_1 B_3 A_1 R_4 + B_1 R_4 A_2^2 R_1 B_5 + R_3 A_3 B_3^2 R_2 A_1 - A_3 A_1 B_5 R_1 B_3 \\
& - A_3^2 B_1^2 - R_3 A_3 B_3 A_1 B_5 - A_3 B_1 R_2 B_3 A_1 + A_3 B_3^2 R_1 A_1 R_4 - A_3 B_1 R_1 A_2 B_5 \\
& - A_3 B_1 B_3 A_1 R_4 - R_3 A_3 A_2 B_5 B_1 - R_3 A_3 B_3 R_2 A_2 B_1 - A_3 B_1 R_4 A_2 R_1 B_3 \\
& + R_2 A_2^2 B_6 B_1 R_3 - R_2 A_2 B_6 B_1 A_1 - R_2 A_3 B_3 B_2 A_1 + R_3 A_2^2 B_5 R_2 B_1 \\
& - R_2 B_3 A_1 B_6 R_3 A_2 - R_2 A_2^2 R_4 B_1 B_2 - R_2 B_3 A_1^2 R_4 B_4 - R_2 A_3 A_2 B_1 R_3 B_4 \\
& + R_2 A_2 A_1 R_4 B_3 B_2 + R_2 A_3 A_2 B_1 B_2 + R_2 A_2 R_4 B_4 B_1 A_1 - R_1 B_3 A_3^2 R_3 B_4 \\
& - R_1 B_3 A_3 B_2 R_4 A_2 - R_1 B_3 A_3 A_1 B_6 + R_1 B_3 A_3 A_1 R_4 B_4 + A_1 B_5 B_2 A_3 \\
& - R_3 A_2 B_5 R_2 B_3 A_1 + B_1 R_4 A_2 B_2 A_3 - A_3 R_4 B_4 B_1 A_1 + B_6 A_1 B_5 R_3 A_2 \\
& - R_1 A_2 B_5 A_1 R_4 B_4 + R_2 A_3 B_3 R_3 B_4 A_1 - B_1 A_2 B_5 A_1 R_4 + A_2 A_1 B_5 R_1 B_6 \\
& - A_2^2 R_3 B_5 R_1 B_6 + A_3 A_2 R_3 B_3 R_1 B_6 - A_1 B_5 R_2 A_2 B_1 - B_1 A_3 R_3 A_2 B_6 \\
& - R_1 A_2 B_5 B_2 A_3 + R_1 A_2 B_5 R_3 B_4 A_3 + R_1 A_2^2 B_5 B_2 R_4 - A_1 B_5 R_3 B_4 A_3 \\
& - A_1 B_5 B_2 R_4 A_2 + 2B_3 R_2 A_2 R_4 B_1 A_1 + 2R_3 A_3 A_2 B_5 R_1 B_s) / (-R_3 A_3 \\
& + R_3 R_2 A_2 + R_1 A_3 + A_1 R_4 - R_1 A_2 R_4 - R_2 A_1)(B_4 A_1 B_5 + A_3 B_3 B_2 \\
& - A_3 B_4 B_1 - A_2 B_5 B_2 + A_2 B_6 B_1 - B_3 A_1 B_6). \tag{A.8}
\end{aligned}$$

Appendix B

The Jacobian matrix for the case of three species

For the case of three species, the nine f functions based on (1.5) to (1.13) are given as following:

$$\begin{aligned} f_1 &= (A_1 - A_2R_1)x - (A_1 - A_2R_1)x\alpha - (A_1 - A_2R_1)x\beta + (A_1 - A_2R_1)y\alpha' \\ &\quad + (A_1 - A_2R_1)z\beta' - (B_1 - B_4R_1)\alpha - (B_1 - B_4R_1)\beta + (B_2 - B_5R_1)\alpha' \\ &\quad + (B_3 - B_6R_1)\beta' + B_1 - B_4R_1 = 0 \end{aligned} \tag{B.1}$$

$$\begin{aligned} f_2 &= (A_3 - A_2R_2)x - (A_3 - A_2R_2)x\alpha - (A_3 - A_2R_2)x\beta + (A_3 - A_2R_2)y\alpha' \\ &\quad + (A_3 - A_2R_2)z\beta' - (B_7 - B_4R_2)\alpha - (B_7 - B_4R_2)\beta + (B_8 - B_5R_2)\alpha' \\ &\quad + (B_9 - B_6R_2)\beta' + B_7 - B_4R_2 = 0 \end{aligned} \tag{B.2}$$

$$\begin{aligned} f_3 &= (A_4 - A_2R_3)x - (A_4 - A_2R_3)x\alpha - (A_4 - A_2R_3)x\beta + (A_4 - A_2R_3)y\alpha' \\ &\quad + (A_4 - A_2R_3)z\beta' - (B_{10} - B_4R_3)\alpha - (B_{10} - B_4R_3)\beta + (B_{11} - B_5R_3)\alpha' \\ &\quad + (B_{12} - B_6R_3)\beta' + B_{10} - B_4R_3 = 0 \end{aligned} \tag{B.3}$$

$$\begin{aligned}
f_4 = & (A_1 - A_2R_4)x\alpha + (A_1 - A_2R_4)y - (A_1 - A_2R_4)y\gamma - (A_1 - A_2R_4)y\alpha' \\
& +(A_1 - A_2R_4)z\gamma' + (B_1 - B_4R_4)\alpha - (B_2 - B_5R_4)\gamma - (B_2 - B_5R_4)\alpha' \\
& +(B_3 - B_6R_4)\gamma' + B_2 - B_5R_4 = 0
\end{aligned} \tag{B.4}$$

$$\begin{aligned}
f_5 = & (A_3 - A_2R_5)x\alpha + (A_3 - A_2R_5)y - (A_3 - A_2R_5)y\gamma - (A_3 - A_2R_5)y\alpha' \\
& +(A_3 - A_2R_5)z\gamma' + (B_7 - B_4R_5)\alpha - (B_8 - B_5R_5)\gamma - (B_8 - B_5R_5)\alpha' \\
& +(B_9 - B_6R_5)\gamma' + B_8 - B_5R_5 = 0
\end{aligned} \tag{B.5}$$

$$\begin{aligned}
f_6 = & (A_4 - A_2R_6)x\alpha + (A_4 - A_2R_6)y - (A_4 - A_2R_6)y\gamma - (A_4 - A_2R_6)y\alpha' \\
& +(A_4 - A_2R_6)z\gamma' + (B_{10} - B_4R_6)\alpha - (B_{11} - B_5R_5)\gamma - (B_{11} - B_5R_5)\alpha' \\
& +(B_{12} - B_6R_5)\gamma' + B_{11} - B_5R_5 = 0
\end{aligned} \tag{B.6}$$

$$\begin{aligned}
f_7 = & (A_1 - A_2R_7)x\beta + (A_1 - A_2R_7)y\gamma + (A_1 - A_2R_7)z - (A_1 - A_2R_7)z\beta' \\
& -(A_1 - A_2R_7)z\gamma' + (B_1 - B_4R_7)\beta + (B_2 - B_5R_7)\gamma - (B_3 - B_6R_7)\beta' \\
& -(B_3 - B_6R_7)\gamma' + B_3 - B_6R_7 = 0
\end{aligned} \tag{B.7}$$

$$\begin{aligned}
f_8 = & (A_3 - A_2R_8)x\beta + (A_3 - A_2R_8)y\gamma + (A_3 - A_2R_8)z - (A_3 - A_2R_8)z\beta' \\
& -(A_3 - A_2R_8)z\gamma' + (B_7 - B_4R_8)\beta + (B_8 - B_5R_8)\gamma - (B_9 - B_6R_8)\beta' \\
& -(B_9 - B_6R_8)\gamma' + B_9 - B_6R_8 = 0
\end{aligned} \tag{B.8}$$

$$\begin{aligned}
f_9 = & (A_4 - A_2R_9)x\beta + (A_4 - A_2R_9)y\gamma + (A_4 - A_2R_9)z - (A_4 - A_2R_9)z\beta' \\
& -(A_4 - A_2R_9)z\gamma' + (B_{10} - B_4R_9)\beta + (B_{11} - B_5R_9)\gamma - (B_{12} - B_6R_9)\beta' \\
& -(B_{12} - B_6R_9)\gamma' + B_{12} - B_6R_9 = 0,
\end{aligned} \tag{B.9}$$

where

- $A_1 = {}^{50}A_x, A_2 = {}^{52}A_x, A_3 = {}^{53}A_x, A_4 = {}^{54}A_x$
- $B_1 = {}^{50}A_s^{III}C_s^{III}W_s^{III}, B_2 = {}^{50}A_s^{VI}C_s^{VI}W_s^{VI}, B_3 = {}^{50}A_s^{IX}C_s^{IX}W_s^{IX}$
- $B_4 = {}^{52}A_s^{III}C_s^{III}W_s^{III}, B_5 = {}^{52}A_s^{VI}C_s^{VI}W_s^{VI}, B_6 = {}^{52}A_s^{IX}C_s^{IX}W_s^{IX}$

- $B_7 = {}^{53}A_s^{III}C_s^{III}W_s^{III}, B_8 = {}^{53}A_s^{VI}C_s^{VI}W_s^{VI}, B_9 = {}^{53}A_s^{IX}C_s^{IX}W_s^{IX}$
- $B_{10} = {}^{54}A_s^{III}C_s^{III}W_s^{III}, B_{11} = {}^{54}A_s^{VI}C_s^{VI}W_s^{VI}, B_{12} = {}^{54}A_s^{IX}C_s^{IX}W_s^{IX}$.

So the Jacobian matrix is given as follows

$$\begin{aligned}
J &= \begin{pmatrix} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} & \frac{\partial f_1}{\partial z} & \frac{\partial f_1}{\partial \alpha} & \frac{\partial f_1}{\partial \beta} & \frac{\partial f_1}{\partial \gamma} & \frac{\partial f_1}{\partial \alpha'} & \frac{\partial f_1}{\partial \beta'} & \frac{\partial f_1}{\partial \gamma'} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} & \frac{\partial f_2}{\partial z} & \frac{\partial f_2}{\partial \alpha} & \frac{\partial f_2}{\partial \beta} & \frac{\partial f_2}{\partial \gamma} & \frac{\partial f_2}{\partial \alpha'} & \frac{\partial f_2}{\partial \beta'} & \frac{\partial f_2}{\partial \gamma'} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{\partial f_9}{\partial x} & \frac{\partial f_9}{\partial y} & \frac{\partial f_9}{\partial z} & \frac{\partial f_9}{\partial \alpha} & \frac{\partial f_9}{\partial \beta} & \frac{\partial f_9}{\partial \gamma} & \frac{\partial f_9}{\partial \alpha'} & \frac{\partial f_9}{\partial \beta'} & \frac{\partial f_9}{\partial \gamma'} \end{pmatrix} \\
&= \begin{pmatrix} E_{1p} & E_1\alpha' & E_1\beta' & -E_1x-F_1 & -E_1x-F_1 & 0 & E_1y+G_1 & E_1z+H_1 & 0 \\ E_{2p} & E_2\alpha' & E_2\beta' & -E_2x-F_2 & -E_2x-F_2 & 0 & E_2y+G_2 & E_2z+H_2 & 0 \\ E_{3p} & E_3\alpha' & E_3\beta' & -E_3x-F_3 & -E_3x-F_3 & 0 & E_3y+G_3 & E_3z+H_3 & 0 \\ E_4\alpha & E_4q & E_4\gamma' & E_4x+F_4 & 0 & -E_4y-G_4 & -E_4y-G_4 & 0 & E_4z+H_4 \\ E_5\alpha & E_5q & E_5\gamma' & E_5x+F_5 & 0 & -E_5y-G_5 & -E_5y-G_5 & 0 & E_5z+H_5 \\ E_6\alpha & E_6q & E_6\gamma' & E_6x+F_6 & 0 & -E_6y-G_6 & -E_6y-G_6 & 0 & E_6z+H_6 \\ E_7\beta & E_7\gamma & E_7r & 0 & E_7x+F_7 & E_7y+G_7 & 0 & -E_7z-H_7 & -E_7z-H_7 \\ E_8\beta & E_8\gamma & E_8r & 0 & E_8x+F_8 & E_8y+G_8 & 0 & -E_8z-H_8 & -E_8z-H_8 \\ E_9\beta & E_9\gamma & E_9r & 0 & E_9x+F_9 & E_9y+G_9 & 0 & -E_9z-H_9 & -E_9z-H_9 \end{pmatrix} \quad (\text{B.10})
\end{aligned}$$

where

- $E_1 = A_1 - A_2R_1, F_1 = B_1 - B_4R_1, G_1 = B_2 - B_5R_1, H_1 = B_3 - B_6R_1$
- $E_2 = A_3 - A_2R_2, F_2 = B_7 - B_4R_2, G_2 = B_8 - B_5R_2, H_2 = B_9 - B_6R_2$
- $E_3 = A_4 - A_2R_3, F_3 = B_{10} - B_4R_3, G_3 = B_{11} - B_5R_3, H_3 = B_{12} - B_6R_3$
- $E_4 = A_1 - A_2R_4, F_4 = B_1 - B_4R_4, G_4 = B_2 - B_5R_4, H_4 = B_3 - B_6R_4$
- $E_5 = A_3 - A_2R_5, F_5 = B_7 - B_4R_5, G_5 = B_8 - B_5R_5, H_5 = B_9 - B_6R_5$
- $E_6 = A_4 - A_2R_6, F_6 = B_{10} - B_4R_6, G_6 = B_{11} - B_5R_6, H_6 = B_{12} - B_6R_6$
- $E_7 = A_1 - A_2R_7, F_7 = B_1 - B_4R_7, G_7 = B_2 - B_5R_7, H_7 = B_3 - B_6R_7$
- $E_8 = A_3 - A_2R_8, F_8 = B_7 - B_4R_8, G_8 = B_8 - B_5R_8, H_8 = B_9 - B_6R_8$
- $E_9 = A_4 - A_2R_9, F_9 = B_{10} - B_4R_9, G_9 = B_{11} - B_5R_9, H_9 = B_{12} - B_6R_9$
- $p = 1 - \alpha - \beta, q = 1 - \gamma - \alpha', r = 1 - \beta' - \gamma'$.

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