

Argentometric chloride determination by inductively coupled plasma-optical emission spectroscopy in a wide range of sample matrices

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Supporting Information

Contents:

t-test for comparison of the means of two measurements	S2
Theoretical LOQ measurement	S2
Working range LOD and LOQ	S3
Complete AgCl formation by DLS	S4
Stability of calibration solutions	S4
References	S5

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t-test for comparison of the means of two measurements

A statistical test was used to determine whether the difference between two measurements is significant¹. The measurements could be under different conditions, of different samples, or using two different methods. The null hypothesis of the test is that the two measurements give the same result.

First, the pooled standard deviation is calculated using the equation:

$$s = \sqrt{\frac{(n_i - 1)s_i^2 + (n_j - 1)s_j^2}{n_i + n_j - 2}}$$

Where n_i and n_j are the numbers of repeated measurements in measurements i and j, and s_i and s_j are the standard deviations of measurements i and j. Since only three measurements were made, the standard deviation was calculated using the precision of the measurement method. The argentometric ICP-OES measurements have a precision of 1% (based on the relative standard deviation of Ag^+ measurements, at a 95% confidence level), while the ion chromatography measurements have a precision of 2.89%².

Once the pooled standard deviation has been calculated, it can be used in the following equation:

$$t = \frac{\bar{x}_i - \bar{x}_j}{s \sqrt{\frac{1}{n_i} + \frac{1}{n_j}}}$$

Where \bar{x}_i and \bar{x}_j are the averages of measurement sets i and j. The calculated t value is then compared to the critical t value¹ for i measurements, at a 95% confidence level. If the value of t is smaller than the critical value, the difference between the two measurements can be considered insignificant.

Theoretical LOQ measurement

The LOQ concentration of the method was calculated for different initial Ag^+ concentrations. It was determined that the lowest LOQ value of the method, ca. 0.1 mg L⁻¹, could be obtained using an initial Ag^+ concentration of 14.32 mg L⁻¹. To confirm this finding, two calibration curves were plotted, one using an initial Ag^+ concentration of 14.32 mg L⁻¹, and one using 50 mg L⁻¹. Both curves were prepared using calibration solutions with concentrations of 0.1, 0.15, 0.25, 0.3, 0.5, and 0.75 mg L⁻¹ chloride (figure S1). It can be observed that measurements using 14.32 mg L⁻¹ Ag^+ resulted in a linear curve beginning at 0.1 mg L⁻¹ chloride. On the other hand, for measurements using 50 mg L⁻¹ Ag^+ , a linear relation was not observed for Cl^- concentrations below 0.25 mg L⁻¹ (to highlight this, some additional Cl^- measurements are presented). These results confirm the theoretically calculated LOQ values for these Ag^+ concentrations.

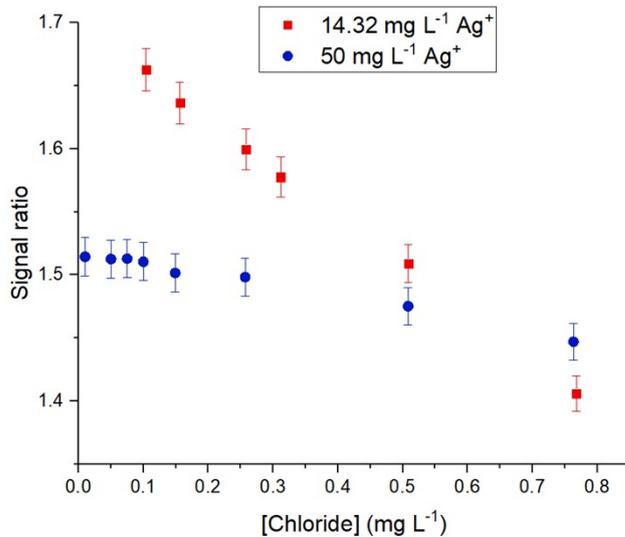


Figure S1: Calibration curves when an initial Ag⁺ concentration of 14.32 (red squares) and 50 (blue circle) mg L⁻¹ are used.

Working range LOD and LOQ

An initial Ag⁺ concentration of 50 mg L⁻¹ was chosen as the optimal value for the method, for a working range of 0.2-16 mg L⁻¹. In order to determine the method LOD and confirm the theoretical LOQ value (0.2 mg L⁻¹) samples of Cl⁻ (0-1 mg L⁻¹) were measured. When concentrations past the methods' LOQ are measured, the relation between neighboring measurements should become linear. Since the second derivative of a linear function is zero, the second derivative of the measurement results should become zero once the LOQ value has been reached. The first and second derivatives of the measured results were obtained

$$\frac{\Delta y}{\Delta x}$$

by calculating $\frac{\Delta y}{\Delta x}$ (wherein y represents the measured intensity, and x the Cl⁻ concentration). The results of the measurements were plotted, along with their second derivative (figure S2), revealing a LOD concentration of 0.075 mg L⁻¹ and confirming the theoretical LOQ concentration of 0.2 mg L⁻¹.

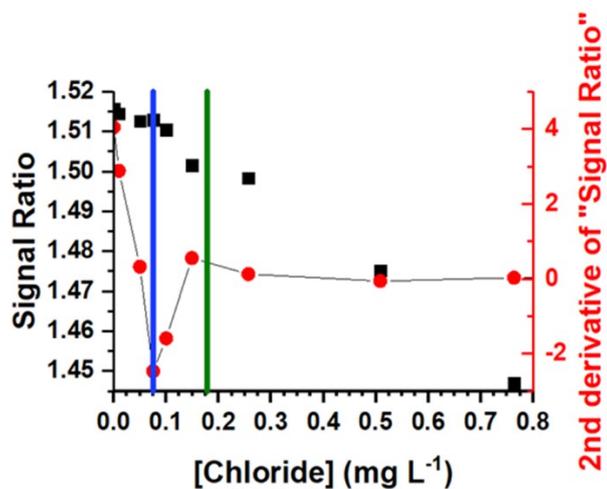


Figure S2. Results for 0-1 mg L⁻¹ Cl⁻ samples. Ag⁺/Y⁺ ratio is marked with black squares, the second derivative is marked with red circles, and the LOD and LOQ of the method are marked with blue and green lines, correspondingly.

Complete AgCl formation by DLS

Results for samples filtered at different times (relative to Ag⁺ addition) indicate AgCl formation is complete within five minutes of Ag⁺ addition. The rapid formation of AgCl was supported by DLS measurements. Measurements of 10 mg L⁻¹ Cl⁻, five and thirty minutes after Ag⁺ addition, gave hydrodynamic radius values of 124.9±0.2 and 135.4±0.5, correspondingly. The negligible difference between the two measurements provides additional support that the AgCl particles have completed their growth within five minutes of the Ag⁺ addition.

Method Selectivity

The selectivity of the method was examined by measuring a solution containing 4 mg L⁻¹ of chloride twice; once as-is and once in the presence of eight common "impurity" elements (Mn, Fe, Mg, Ca, Cu, Pb, Zn, Al). A sample of the impurities with no chloride was also measured. The differences between the two measurements were found to be statistically insignificant. The measurement results are presented in table S1.

Table S1. Selectivity measurements results

	Zn	Pb	Mn	Mg	Fe	Cu	Ca	Al	Cl
Impurities without chloride	3.90	3.92	3.90	3.94	3.91	3.98	4.01	4.01	-
Impurities with chloride	3.90	3.92	3.88	3.93	3.89	3.96	3.99	4.00	4.00
Chloride without impurities	-	-	-	-	-	-	-	-	4.06

Stability of calibration solutions

Calibration solutions were kept (in the dark) after they have been used to plot a calibration curve. After two weeks passed, the solutions were used to plot a calibration curve again. If any changes in the amount of Ag⁺ in the solutions take place, either the slope or intercept of the calibration curve should change accordingly. Since the two calibration curves are nearly identical (figure S3), it can be concluded that Ag⁺ concentration does not change further after the samples have been filtered.

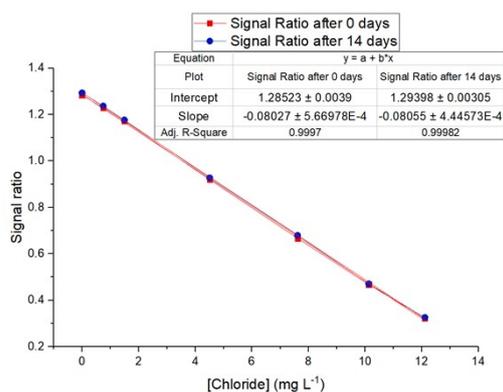


Figure S3: Calibration curves plotted using calibration solutions 0 (red squares) and 14 (blue circles) days after filtration.

Comparison to direct Cl⁻ determination by ICP-OES

ICP-OES instruments using vacuum or purged optical systems can measure chloride directly at the wavelength of 134.72 nm. Reviewing the literature, LODs for such methods range from 0.012 to 0.9 mg·L⁻¹, while the LOQ is usually not detailed. Examples of LODs of published methods are presented in table S2. The argentometric method, which can be applied to any ICP-OES instrument, has a LOD of 0.075 mg·L⁻¹, which is similar to the values obtained by direct measurement. It should be noted that the LODs presented are for specific methods, and some require matrix-matching³, which the argentometric method does not.

Table S2. LODs for ICP-OES determination of Cl⁻

Title	LOD
Low-level determination of non-metals (Cl, Br, I, S, P) in waste oils by inductively coupled plasma optical emission spectrometry using prominent spectral lines in the 130–190 nm range	0.9 ⁴
Use of a charge-coupled device detector in the 120±190 nm range in axially-viewed inductively coupled plasma atomic emission spectrometry	0.05-0.12 ³
Analysis of biodiesel by argon–oxygen mixed-gas inductively coupled plasma optical emission spectrometry	0.4 ⁵
Determination of chlorine, bromine and iodine in milk samples by ICP-OES	0.8 ⁶
Chloride analysis of botanical samples by ICP-OES	0.041 ⁷
Feasibility of Microwave-Induced Combustion for Digestion of Crude Oil Vacuum Distillation Residue for Chlorine Determination	0.015 ⁸
Chlorine and sulfur determination in extra-heavy crude oil by inductively coupled plasma optical emission spectrometry after microwave-induced combustion	0.012 ⁹
Application of prominent spectral lines in the 125–180 nm range for inductively coupled plasma optical emission spectrometry	0.019 ¹⁰

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