# Determination of Beryllium in the Parts-per-Billion Range in Three Standard Reference Materials by Inductively Coupled Plasma Atomic Emission Spectrometry

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**This paper provides a method to directly determine beryllium in the parts-per-billion range in three standard reference materials by inductively coupled plasma (ICP) emission spectroscopy. Wavelength selection and instrument operating parameters were studied. It was found that the most sensitive wavelength, 313.04 nm, of beryllium is located between two unknown peaks, probably due to the OH molecule. Because of the spectral interference from the unknown peaks it is impossible to determine the beryllium in the sub-parts-per-billion range using the 313.04-nm analytical line. Iron, as present in biological samples, has severe spectral interferences on the Be 234.86-nm line. Due to these effects the emission line at 313.11 nm was selected as the analytical line for Be. The results obtained by the standard addition method and the calibration curve in aqueous solution were compared with the certified value of one standard reference material. The slopes of the two curves were equal. The content of Be in NBS 1571 (orchard leaves) was determined to be 0.0143 μg/g, which is different from the certified value 0.027 μg/g.**

In recent years, the toxicity of beryllium and beryllium compounds to humans has been recognized. A relatively low intake of beryllium can lead to acute or chronic diseases (*1–4*). It is important to establish an analytical method which can be used for environmental research and as a diagnostic tool to determine the amount of beryllium in biomedical and environmental samples. On the basis of such information, the function of beryllium in biology and medicine can be verified. Because of the very low content of beryllium in biological samples and the complicated matrix, it is difficult to determine rapidly trace amounts of beryllium in biological samples. A search of the literature revealed that the most extensively used method to determine trace amounts of beryllium is graphite furnace AAS (GFAAS) (*5–14*). But the sensitivity of GFAAS is not sufficient enough to directly determine trace amounts of beryllium in biological samples. Some pretreatments must be used to enrich the beryllium and to separate it from other interferent elements. These pretreatments include extraction by acetyl acetone–MIBK and coprecipitation by lanthanum. Additionally, the surface state of graphite tube has influence on the determination of beryllium. The tube should be treated by some elements such as zirconium or lanthanum to form a carbide to increase the sensitivity. This is a laborious and time-consuming method for environmental research.

The ICPAES is now a well-established analytical method and one of the most promising new analytical techniques because of its high sensitivity and low level of interferences. This paper describes a method to directly determine trace amounts of beryllium in three standard reference materials.

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## EXPERIMENTAL SECTION

**Instrumentation.** The following ICP instrumentation is employed: a sequential ICP spectrometer, Model JY-38 P (Instruments S.A.), with a 1-m focal length Czerny-Turner spectrometer and an ICP device (Plasma-Therm, Inc.) with a HF generator of 1.5 kW at 27.12 MHz. A holographic grating with 2400 grooves/mm provides a reciprocal linear dispersion of 0.4 nm/mm and spectral resolution of 0.02 nm in first order. A quartz torch (three concentric tube design) and a modified cross-flow nebulizer (steel mounted with a Pt/Ir capillary) (Instruments S.A.) are used. The solution feed rate, controlled by a peristaltic pump, is 0.9 mL/min (*15*). A DEC PDP 11/03 computer with RX 02 dual floppy disk and software developed by Instruments S.A. is used for the evaluation of the data and for the determination of background and net peak height. The special parameters used for evaluation of the net peak height are shown in Figure 1.

These parameters are defined as follows: NTS, number of totally measured steps (the step width is 0.002 nm in all cases) (30 steps in this case); NSL, number of steps on the left side of $\lambda$ (starting point for scanning the peak) (10 steps in this case); NSP, number of steps for searching the true peak position (7 steps); NNSL, number of neglected steps at the low wavelength side of $\lambda$ (0 step); NNSR, number of neglected steps at the high wavelength side of $\lambda$ (15 steps); $\lambda$, preselected peak wavelength.

From the measurement on the position of NNSL and NNSR the background on the low and high wavelength side of $\lambda$ can be determined. The net peak height is calculated from the formula

$$R = \text{peak mes} - \left(\frac{\text{BGR mes} + \text{BGL mes}}{2}\right)$$

in which peak mes is the intensity of peak measurement, BGR mes is the intensity of background measurement at NNSR, and BGL mes is the intensity of background measurement at NNSL. If NNSL is set to 0, $R$ = peak mes − BGR mes.

The power input to the plasma is constant 55% of generator output power (about 0.85 kW). The outer argon gas rate (coolant gas) is 9.0 L/min. The inner argon gas rate (aerosol carrier gas) is about 0.7 L/min. The gas pressure on nebulizer is 1.9 bar.

**Sample Materials.** For testing of the method the following standard reference materials have been used: bovine liver (NBS 1577), orchard leaves (NBS 1571), and ripariodes (Reference Material (RM) No. 61, Commission of the European Community (under certification). It is an aquatic plant).

**Standard and Calibration.** The set of standards in 1% $NHO_3$ (v/v) obtained by the progressive dilution of 1000 ppm stock solution results in a two-point calibration: 1 ppb and 5 ppb. When the standard addition method is used, 0.5 g of SRM of NBS and 0.1 g of RM, No. 61, are weighed in triplicate in quartz digestion tubes. Before and after digestion, 10 and 20 ng of beryllium (20 and 40 ng for RM, No. 61) are added to the two tubes, respectively (total amount of sample solution, 10 mL). The results are obtained by the extrapolated line intercept.

**Sample Preparation Method.** Approximately 0.5 g of the samples are weighed into quartz digestion tubes. Three milliliters of subboiling distilled concentrated nitric acid is added to each tube. The tubes are put into an autoclave (*16*). The whole device is then placed in a temperature-controlled heating block. Samples are digested at 160 °C for 6 h. After being cooled, the digested

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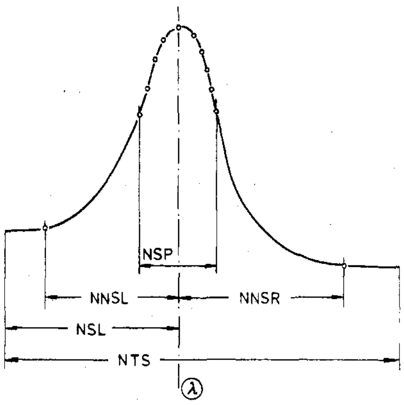


**Figure 1.** Software parameters for evaluating the net peak height.

Table I. Wavelength for the Determination of Beryllium (*18*)

| symbol | wavelength, nm | $S/B^a$ | concn, ppm | det limit, ppm |
|---|---|---|---|---|
| Be(II) | 313.042 | 110 | 1.0 | 0.000 27 |
| Be(I) | 234.861 | 96 | 1.0 | 0.000 31 |
| Be(II) | 313.107 | 41 | 1.0 | 0.000 73 |
| Be(I) | 249.473 | 8 | 1.0 | 0.003 8 |
| Be(I) | 265.045 | 6 | 1.0 | 0.004 7 |

[a] Signal to background ratio.

samples are rinsed into 10-mL volumetric flasks and diluted to volume with redistilled water. The results are obtained by comparing the signal of the sample with the calibration curve in aqueous solution and by the extrapolated line intercept. The slopes of the two curves are compared to check whether the two curves are parallel. When the combustion in a stream of oxygen method is used (*17*), 0.25 g of sample is burned and digested in 2 mL of concentrated nitric acid and finally diluted to 5 mL.

## RESULTS AND DISCUSSION

The wavelengths usually used to determine beryllium are given in Table I. From Table I Be 313.04 nm and Be 234.86 nm are the lines that have priority over others due to the higher line to background ratios and the lower detection limit. From the scanning graphical display, Figure 2a, it can be seen that there are two unknown peaks on each side of the Be 313.04 nm line contributed by the OH molecule (*18*). When the concentration of beryllium is high, these two peaks cannot be seen (Figure 2b). When the concentration of beryllium is below 5 ppb, it is obviously shown that the peak due to beryllium is convoluted with the interfering spectra. Therefore it is difficult to determine the beryllium in the sub-parts-per-billion range when the Be 313.04 nm line is used. When the Be 234.86 nm line and its near lines from the wavelength table (*19*) are considered, it can be found that there is a strong iron line at 234.83 nm, near the Be 234.86 nm line. If 0.5 g of biological samples is weighed and the digested solution diluted to 10 mL, the concentration of iron in the final solution can be greater than 10 ppm. From a scan of the Be 234.86 nm line, Figure 3, it can be seen that there is a severe spectral interference produced by the wing of Fe 234.83 nm line. Therefore it is also impossible to directly determine the content of beryllium in biological samples without taking the iron overlap into consideration. At last, Be 313.11 nm is selected as the analytical line. From the scans near the Be 313.11 nm line in the three samples mentioned above it can be seen that there is a peak on the low wavelength side of the Be 313.11 nm line in orchard leaves and ripariodes (Figure 4). This peak is ascribed to titanium present in these samples. Taking this into consideration, background correction is done only on the high wavelength side of the Be 313.11 nm line in a distance of 0.03 nm.

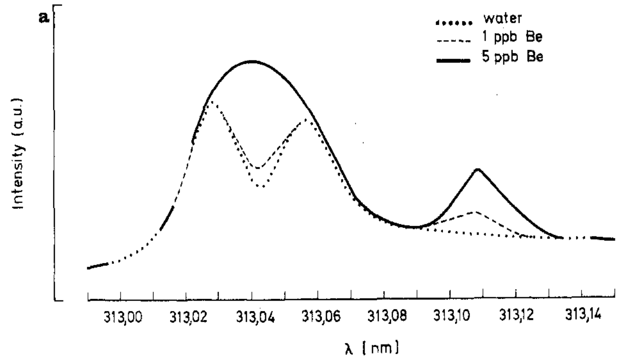


**Figure 2.** Spectral scan near Be 313.042 nm at (a) 5 ppb and (b) 500 ppb.

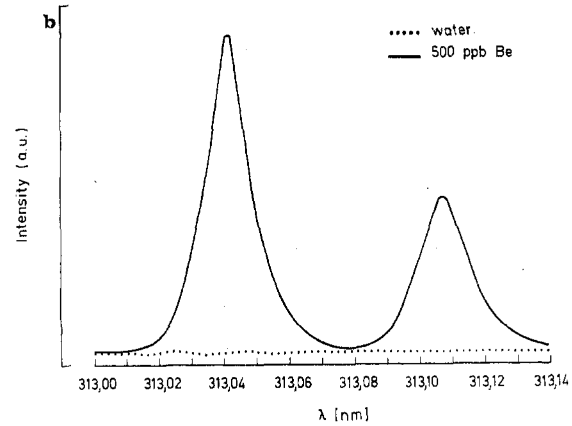


**Figure 3.** Spectral scan near Be 234.861 nm.

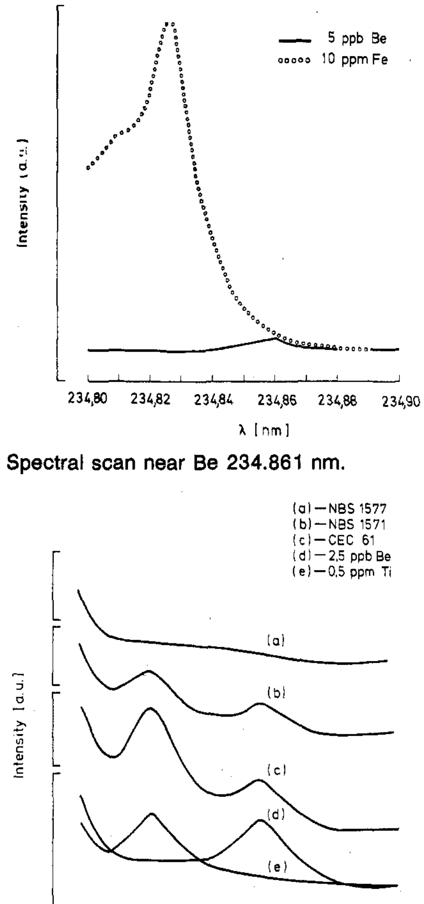


**Figure 4.** Spectral scan near Be 313.1072 nm in different reference samples.

Table II. The Comparison of Slopes between the Linear Regression Curve in 1% $HNO_3$ Solution and the Linear Regression Curve of Standard Addition Method

| sample name | regression eq ($C = A + (B \times 10^{-4} I)$)[a] calibration curve in 1% $HNO_3$ intercept ($A$) | slope ($B$) | std addition curve intercept ($A$) | slope ($B$) |
|---|---|---|---|---|
| NBS 1571 (about 0.5 g in 10 mL) | −0.441 | 0.95 | −0.717 | 0.91 |
| NBS 1577 (about 0.5 g in 10 mL) | −0.375 | 1.12 | −0.0175 | 1.09 |
| | −0.313 | 0.75 | −0.172 | 0.78[b] |
| CEC 61 (about 0.1 g in 10 mL) | −0.896 | 1.42 | −1.72 | 1.37 |

[a] $C$, concentration in ppb; $I$, intensity. [b] The combustion method in a stream of oxygen is used (*17*); 0.25 g of sample is digested in 5 mL.

Table III. Recovery

| sample name | weight, g | ng of Be measd in sample | ng of Be added ($n$ = 2)[a] before digestion | after digestion | ng of Be measd with spike ($n$ = 2) before digestion | after digestion | % recovery with spike ($n$ = 2) before digestion | after digestion |
|---|---|---|---|---|---|---|---|---|
| orchard leaves (NBS 1571) | 0.5008 ($n$ = 2) | 6.5 | 10 | 10 | 14.4 | 15.9 | 79 | 94 |
| | | | 20 | 20 | 25.2 | 25.1 | 94 | 93 |
| | 0.4999 ($n$ = 2) | 7.8 | 10 | 10 | 17.4 | 16.3 | 96 | 85 |
| | | | 20 | 20 | 27.0 | 27.2 | 96 | 97 |
| | 0.5003 ($n$ = 2) | 7.5 | | 10 | | 18.1 | | 106 |
| | | | | 20 | | 28.3 | | 104 |
| bovine liver (NBS 1577) | 0.5001 ($n$ = 2) | ⩽det limit | 10 | 10 | 9.8 | 9.2 | 98 | 92 |
| | | | 20 | 20 | 20.3 | 20.6 | 102 | 103 |
| | 0.5003 ($n$ = 2) | ⩽det limit | 10 | 10 | 8.4 | 9.7 | 84 | 97 |
| | | | 20 | 20 | 19.1 | 20.3 | 96 | 102 |
| | 0.5006 ($n$ = 2) | ⩽det limit | | 10 | | 10.4 | | 104 |
| | | | | 20 | | 21.4 | | 107 |
| | 0.2502[b] ($n$ = 2) | ⩽det limit | | 10 | | 10.0 | | 100 |
| | | | | 20 | | 18.5 | | 93 |
| Ripariodes (CEC 61) | 0.1000 ($n$ = 2) | 20.7 | 20 | 20 | 44.0 | 41.5 | 116 | 104 |
| | | | 40 | 40 | 70.1 | 64.3 | 123 | 109 |
| | 0.1003 ($n$ = 2) | 18.7 | | 20 | | 41.5 | | 114 |
| | | | | 40 | | 65.3 | | 116 |
| | 0.1004 ($n$ = 2) | 20.4 | | 20 | | 42.8 | | 112 |
| | | | | 40 | | 66.4 | | 115 |

[a] $n$ is the number of replicates. [b] The combustion method in a stream of oxygen is used (*17*).

Table IV. Analytical Results of Standard Reference Materials

| sample name | Be content ± std dev, μg/g using calibration curve in 1% $HNO_3$ | using std addition method | certified concn, μg/g |
|---|---|---|---|
| orchard leaves (NBS 1571) | 0.0148 ± 0.0016 ($n$ = 11) | 0.0137 ± 0.0018 ($n$ = 11) | 0.027 ± 0.010 |
| bovine liver (NBS 1577) | ⩽0.003 ± 0.001 ($n$ = 8) | 0.003 ± 0.001 ($n$ = 8) | 0.017[a] |
| ripariodes (CEC 61) | 0.199 ± 0.012 ($n$ = 7) | 0.183 ± 0.014 ($n$ = 7) | no certified |

[a] An information value.

In Table II, the slope of the linear regression curve in 1% $HNO_3$ (v/v) solution is compared with that of the standard addition method. The slopes of the two curves are 0.948 and 0.913 in NBS 1571, 1.12 and 1.09 in NBS 1577, and 1.42 and 1.37 in CEC 61, respectively. Because these sets of curves are obtained on different dates, the sensitivities are different. It can be seen that the slopes of the linear regression curve in 1% $HNO_3$ solution and that of standard addition method are essentially equal.

The analytical method is examined by spiking the three sample matrices with known concentrations of beryllium before and after the digestion step. It is well-known that the precision and accuracy values associate with sample preparation and analytical performance. The recovery data from the digested samples, which are used to check on the measurement technique, are shown in Table III. The average recoveries in NBS 1571 and 1577 and CEC 61 are 97, 99, and 111%, respectively. In addition, the recovery data from the undigested samples, which are used to check whether beryllium is lost in the digestion step, are also included in Table III. The average recoveries in NBS 1571 and 1577 and CEC 61 are 91, 95, and 119%, respectively. We also use the newly developed combustion method (*17*) to measure the Be content in NBS 1577, the results are shown in Tables II and III. The recoveries indicate the validity of the method.

The detection limit is defined as the concentration that gives a signal to twice of the standard deviation of the background signal at the sample wavelength. In this work, the detection limit is 0.15 ± 0.06 ppb ($n$ = 18) when the solution of 1 ppb Be is used as standard solution.

The final results are shown in Table IV. The content of beryllium in NBS 1571 and CEC 61 was determined to be 0.0143 μg/g, which is different from the certified value 0.027 μg/g, and 0.191 μg/g, respectively. The content of beryllium in NBS 1577 was not verified. From the detection limit one can assume that the Be content in this material is ≤0.003 ± 0.001 μg/g.

## CONCLUSION

From the results in Tables II and III, it can be concluded that the Be 313.011 nm line is suitable to determine trace amounts of beryllium in biological samples and the calibration curve in water solution can be conveniently used to determine beryllium. Since there is no ICPAES method to determine beryllium in the specification of SRM of NBS, this work provides a new method to compare with other methods for determination of beryllium at trace levels. The method described here can be used to determine trace amounts of beryllium in biological samples directly, rapidly, and accurately. In trace element analysis by means of ICP, it is important to pay attention to the spectral interference produced by the overlap with nearby broadened line wing like Be 234.861 nm with Fe 234.831 nm and molecular constituents of the plasma itself like the OH band that might be ignored if the element concerned is present in high concentration. The sequential ICP spectrometer provides the flexibility to change the analytical line to avoid spectral interference.

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# Acid Titration of Polar Snow

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**The acidity (or alkalinity) of polar precipitation is a parameter of great interest in the invesitgation of several global geochemical problems. This paper describes the contamination-free sampling and sample handling techniques used and a titration method suitable for determining the ultralow acidity levels of polar precipitation. Test experiments were performed to evaluate the accuracy (±0.2 μequiv L$^{-1}$) of the method in the 0–10 μequiv L$^{-1}$ acidity and alkalinity ranges. These first acidity determinations of Antarctic snow and ancient ice samples illustrate the value of the developed procedure, which could be particularly useful for nearly neutral unbuffered natural water samples such as cloud and rain water collected in remote locations.**

Trace impurities are present in extremely low amounts in central antarctic precipitation (*1*). Concentrations are generally in the micromolar range for the more abundant compounds, i.e., 2 or 3 orders of magnitude less than in rain falling at midlatitudes. It is becoming more and more evident that the analysis of these minute amounts of atmospheric aerosol, when preserved in ice, can reveal important information related to the past global atmosphere (climate, atmospheric circulation, volcanism, etc.) (*2, 3*).

It has recently been shown that the anions $SO_4^{2-}$, $NO_3^-$, and $Cl^-$ are the main soluble impurities which can be detected in snow at the South Pole (*4*). The respective amounts of the counterions (cations) linked with these anions is still open to discussion. For example, it is uncertain whether recent snow and ancient polar ice is acid or alkaline. Very few reliable pH determinations (*5, 6*) and no direct acidity measurements of polar precipitation have been made until now. The exact concentration of the protons is needed to establish the ionic balance of polar snow. In this paper, we describe contamination-free techniques for collecting the samples and for measuring the low acidities (or alkalinities) of polar precipitation. In fact, the acidity of snow is different than the acidity of its meltwater (in which the pH is determined) because the ultrapure snow meltwater readily dissolves $CO_2$ from the ambient atmosphere and from bubbles in the ice. The weak carbonic acid formed significantly modifies the initial acidity (or alkalinity) of the meltwater. The pH value obtained does not therefore offer a satisfactory description of the $H^+$ amounts present in the snow sample. An accurate correction for the excess $H^+$ due to carbonic acid is possible if the ambient atmospheric $CO_2$ content is known. This is rarely the case in a laboratory where variable $CO_2$ contents (often twice the normal background) are common. Classical methods do exist to eliminate the influence of $CO_2$ but these are time-consuming, e.g., working in a $CO_2$-free atmosphere or extracting $CO_2$ by bubbling an inert gas. Indirect methods may be used for evaluating the acidity of ice (electroconductivity measurements (*6*)) or of rain water (charge or conductivity balance (*7*), coulometric titration (*8*)). The method described here is an accurate titration of polar snow (±0.2 μequiv L$^{-1}$ of $H^+$). The pH electrode is used as the selective electrode of the proton. No basic titrant is involved. By addition of small increments of an acid titrant to the sample, a sufficiently low pH range is reached where carbonic acid is essentially undissociated and consequently does not influence the measurements.

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