

# Determination of Magnesium, Calcium and Potassium in Brines by Flame AAS using the SIPS-10 Accessory for Automated Calibration and On-Line Sample Dilution

## Application Note

Atomic Absorption

### Author

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### Introduction

Brines are solutions of sodium chloride containing from 2% to 30% dissolved salt. They are used extensively in industry. The determination of major elements such as magnesium, calcium and potassium in brines by flame atomic absorption spectrometry is relatively simple. There are no chemical interferences, unless phosphates are present. The large concentration of sodium means ionization interferences are absent. Background correction is recommended for magnesium at 285.2 nm because of molecular absorption by sodium chloride.



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Flame atomic absorption spectrometry (AAS) is a very sensitive technique for the determination of the Group 1A and 2A elements. These elements can have very wide ranges of concentration in brines, and may be well above the instrument's calibrated range. It is quite likely some samples would require dilution. If the samples are unknown, a series of dilutions may be necessary. For each dilution, pure sodium chloride must be added for matrix matching. There are other methods to reduce the sensitivity of the instrument. The simplest is to use another wavelength, but Table 1 shows these usually have low intensities for the Group 1A and 2A elements. Another is to rotate the burner head with respect to the light path. An air-acetylene burner at 90 degrees to the light path is about 30 times less sensitive than when the path is coincident with the slot. If the samples are only just out of range then sensitivity may be compromised. Partial burner rotation is not recommended, especially for the Group 1A and 2A elements [1].

Table 1. Relative Sensitivities (1 = Most Sensitive) and Intensities (100 = Most Intense) of Various Absorption Lines [2]

| Element | Wavelength | Relative sensitivity | Relative intensity |
|---------|------------|----------------------|--------------------|
| Ca      | 422.7      | 1                    | 100                |
|         | 239.9      | 200                  | 10                 |
| Mg      | 285.2      | 1                    | 100                |
|         | 202.6      | 30                   | 3                  |
| K       | 766.5      | 1                    | 100                |
|         | 769.9      | 2                    | 80                 |
|         | 404.4      | 400                  | 5                  |

All these methods have the same disadvantages. Another set of standards is required. The samples require at least two measurement passes, one to measure in-range samples and to identify over-range samples and the second to re-measure the over-range samples with the different conditions.

Agilent has introduced a fully automated sample introduction and dilution system for flame AAS, the patented [3] Sample Introduction Pump Systems (SIPS), to avoid all these problems by effectively extending the concentration range without altering instrument conditions or recalibrating the instrument. The innovative design, based on peristaltic pumps, revolutionizes calibration and simplifies the task of over-range sample dilution.

In its simplest configuration, the SIPS-10 (see Figure 1), a specially-designed high-precision peristaltic pump is connected to a T-junction at the inlet to the nebulizer. The peristaltic pump pushes sample solution into the T-junction, which is also connected to a bulk diluent reservoir. This reservoir is a Mariotte bottle to ensure that the aspiration rate of the nebulizer is not affected by the changing level of liquid in the reservoir [4]. With the pump stopped, there is no sample solution flow and the diluent is aspirated by the nebulizer in the conventional way. With the pump running at maximum speed, very little

diluent is aspirated and maximum sensitivity is achieved. Slowing the pump speed results in a reduced flow of sample solution. Since the nebulizer uptake rate is constant, the diluent flow automatically increases to maintain the nebulizer uptake rate, effectively diluting the sample solution. The sample solution flow rate is directly proportional to the speed of the pump. Thus, with accurate computer control of the pump speed, automatic calibration and on-line over-range sample dilution can be achieved.

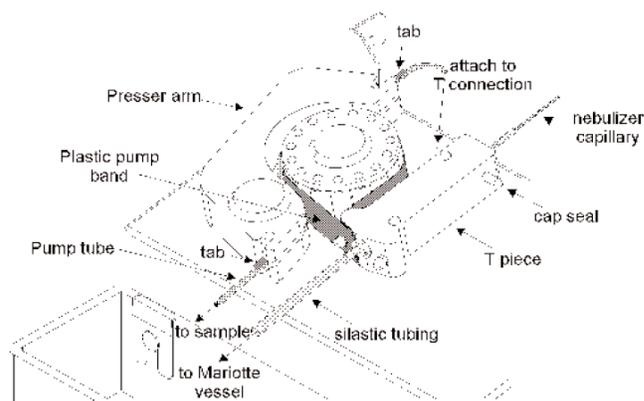


Figure 1. SIPS-10 configuration.

## Benefits of the SIPS System

SIPS increases the dynamic range of flame AA by a factor of 200 so that it now matches the linear dynamic range of ICP-AES. During operation, if the absorbance of a sample is greater than the absorbance of the top standard, the software automatically estimates the dilution factor required to bring the signal within the top half of the calibration graph. The pump is slowed and the over-range sample solution is automatically re-measured at the estimated dilution. This process is continued, if required, until the absorbance of the sample solution is less than the absorbance of the top standard. The dilution-corrected concentration is then reported. SIPS is faster and easier than manual dilution and is highly reproducible.

SIPS not only automatically dilutes over-range samples but also simplifies calibration. With SIPS, only one standard solution is required. SIPS automatically prepares up to 10 calibration points from this one standard by diluting it on-line. With SIPS, the spectrometer can be calibrated much faster than by preparing and measuring manual calibration solutions.

This study compares the results of brine samples which have been diluted manually to those of samples measured using the SIPS.

## Experimental

### Instrumentation

An Agilent SpectrAA-200HT atomic absorption spectrometer with deuterium background correction was used. A Mark VI Universal spraychamber with a Hi-vac nebulizer and a Mark VI air-acetylene burner was used for all elements. The system was optimized for maximum sensitivity with the nebulizer in high solids position [5]. The impact bead was then adjusted one-half turn clockwise to improve the aerosol characteristics [5]. Lamps were standard Agilent hollow cathode lamps for each of the elements. Instrument parameters are summarized in Table 2. The PROMT measurement mode [6] was used with the SIPS-10 accessory to minimize aspiration times whilst ensuring good precisions.

With the SIPS running at maximum speed, the rate of sample solution delivery to the nebulizer is 4.5 mL/ min. The nebulizer uptake rate was measured (using water) at 6.2 mL/min. This ensures that some blank is always aspirated. There is some loss in sensitivity (compared with manual sample introduction), but this has no apparent practical effect.

The samples were also measured using an Agilent Liberty-220 inductively coupled plasma atomic emission spectrometer.

Table 2. Instrument Operating Parameters

| Parameters              | Elements |          |          |
|-------------------------|----------|----------|----------|
|                         | Mg       | Ca       | K        |
| <b>Flame</b>            | Air-Acet | Air-Acet | Air-Acet |
| Wavelength (nm)         | 285.2    | 422.7    | 766.5    |
| Slit (nm)               | 0.5      | 0.5      | 1.0      |
| Delay time (sec)        | 6        | 6        | 6        |
| <b>Manual operation</b> |          |          |          |
| Read time (sec)         | 1        | 1        | 1        |
| Replicates              | 3        | 3        | 3        |
| <b>SIPS</b>             |          |          |          |
| Read delay (sec)        | 6        | 6        | 6        |
| PROMT %Prec             | 1        | 1        | 1        |
| PROMT time (sec)        | 5        | 5        | 5        |
| <b>ICP</b>              |          |          |          |
| Wavelength/nm           | 279.553  | 422.673  | 769.896  |

### SIPS

The single pump SIPS-10 was used. Tests comparing calibration graphs generated with conventional aspiration and with SIPS confirmed that using water as a bulk diluent (not matching the standard and sample matrices) gave inconsistent results, especially at lower absorbance levels. In extreme situations, the calibration graph may display upward curvature. For this reason the bulk diluent was matrix matched to the standards and samples with sodium chloride.

### Reagents

Type 1 water was used as the diluent in preparing standards. All reagents were AR grade.

### Standards

All standards were diluted from commercial 1000 mg/L standards (Merck). Sodium chloride (20 g/L) was added to standards and blank to match the sample concentration. Hydrochloric acid (1 mL of 32% acid/100 mL solution) was added to ensure all solutions had a similar pH.

### Sample Preparation

Samples were supplied as 100 g/L sodium chloride solutions. The three samples were respectively labelled “Low”, “Medium” and “High” to reflect the levels of analyte expected.

An aliquot (10 mL) of each solution was transferred to a 50 mL volumetric flask, hydrochloric acid added as for the standards, and made up to the mark with water. The effective concentration of sodium chloride was 20 g/L.

More dilute solutions were also made to check the accuracy of the SIPS dilution. Smaller aliquots (0.5 mL) of the “Middle” and “High” solutions were treated in the same way. These are labelled “Middle/20” and “High/20” respectively.

A separate set of duplicate solution aliquots from a different sample of the brine would normally be treated in the same way. This was not done in this study because different calibration procedures were being compared. The same solution was read as a duplicate to compare inter-reading variability. The software can automatically calculate the relative percent difference (RPD) between the concentrations of a solution (S) and its paired duplicate (D) as shown in the equation below.

$$RPD = (|S - D|) / ((S + D) / 2) \times 100$$

## Recovery Study

As a suitable reference solution was not available, a recovery study was done using sample "Low". The recovery (%R) of a matrix spike (MSPK) is calculated from the spiked sample result (SSR), the mean sample result (SR) and the spike added (SA) using the equation below. The QC Tests of the SpectrAA software can be set to calculate this value automatically.

$$\%R = (SSR - SR) / SA \times 100$$

If a recovery is between 90% to 110% the calibration graph is considered valid for the sample. A recovery between 40% and 90% indicates some chemical interference. Use of a hotter flame or treatment with a releasing agent may be appropriate in flame AAS. A recovery of less than 40% usually indicates a severe matrix effect, and a standard additions calibration may then be required as well.

## Results and Discussions

Investigations using 100 g/L sodium chloride were done initially. The atomizer and SIPS can cope with this concentration. A concentration of 20 g/L was finally used because the method was more robust for routine determinations.

The analytical results giving the solution concentrations of magnesium, calcium and potassium respectively are reported in Tables 3 to 5. "Manual" refers to samples introduced by the conventional method and over-range samples are flagged as "Over". "Middle/20" and "High/20" were measured without dilution by the SIPS as well.

Table 3. Results for Magnesium in Brine Using SIPS, Manual Dilution and ICP

| Sample    | SIPS-10 | Manual | ICP-AES |
|-----------|---------|--------|---------|
| Low       | 0.0488  | 0.0451 | 0.0408  |
| RPD       | 1.0     | 1.2    |         |
| %R        | 95.3    | 100.2  |         |
| Middle    | 1.515   | 1.553  | 1.532   |
| RPD       | 0.7     | 0.2    |         |
| High      | 11.33   | Over   | 11.21   |
| RPD       | 0.8     | —      |         |
| Middle/20 | 1.677   | 1.687  |         |
| High/20   | 11.14   | 12.00  |         |

The results for magnesium show very good correlation with all techniques. The relative percent differences are very good, as are the recoveries. There is no evidence of any chemical interference.

Table 4. Results for Calcium in Brine Using SIPS, Manual Dilution and ICP

| Sample    | SIPS-10 | Manual | ICP-AES |
|-----------|---------|--------|---------|
| Low       | 0.0425  | 0.0399 | 0.0298  |
| RPD       | 3.4     | 6.4    |         |
| %R        | 99.1    | 98.6   |         |
| Middle    | 6.266   | 6.617  | 6.595   |
| RPD       | 6.7     | 2.1    |         |
| High      | 10.33   | 10.59  | 11.07   |
| RPD       | 0.4     | 0.3    |         |
| Middle/20 | 7.022   | 7.198  |         |
| High/20   | 11.20   | 11.61  |         |

Table 5. Results for Potassium in Brine Using SIPS, Manual Dilution and ICP

| Sample    | SIPS-10 | Manual | ICP-AES |
|-----------|---------|--------|---------|
| Low       | 0.5952  | 0.5979 | 0.5757  |
| RPD       | 2.0     | 0.0    |         |
| %R        | 97.1    | 7      |         |
| Middle    | 0.4977  | 0.4890 | 0.4959  |
| RPD       | 2.9     | 0.5    |         |
| High      | 6.862   | Over   | 6.532   |
| RPD       | 2.8     | —      |         |
| Middle/20 | 0.6947  | 0.5756 |         |
| High/20   | 7.178   | 7.575  |         |

The undiluted results for potassium show very good correlation between the techniques. The manually diluted sample results are not as close as was the case for the other two elements. The most probable explanation is contamination.

The "Low" value by ICP-AES for all elements is reported as being less than by AAS. There is no obvious explanation for this.

The corrected concentrations of the analytes in the solid material are compared in Figures 2, 3 and 4 for magnesium, calcium and potassium respectively.

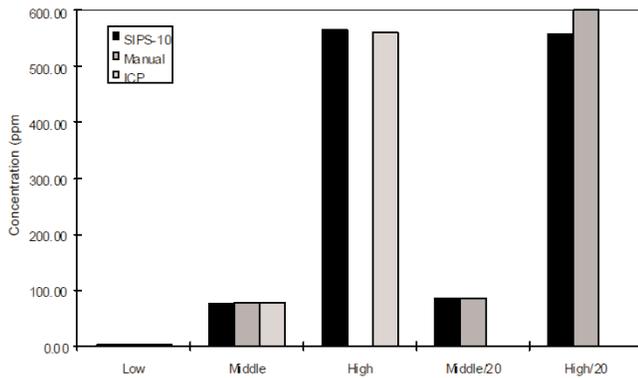


Figure 2. Comparison of the concentrations measured by various techniques of magnesium in solid sodium chloride. The manual result for sample "High" was over-range and is not shown.

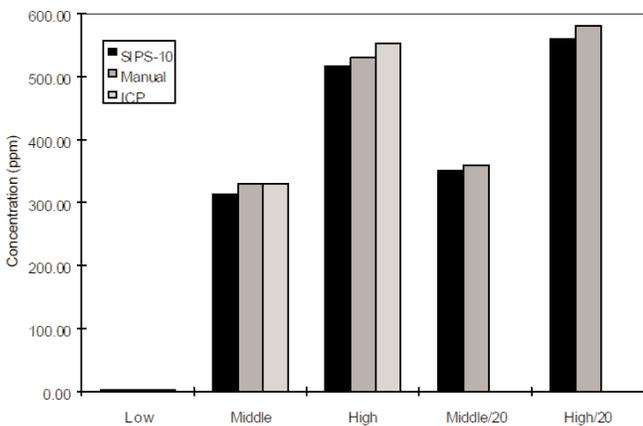


Figure 3. Comparison of the concentrations measured by various techniques of calcium in solid sodium chloride.

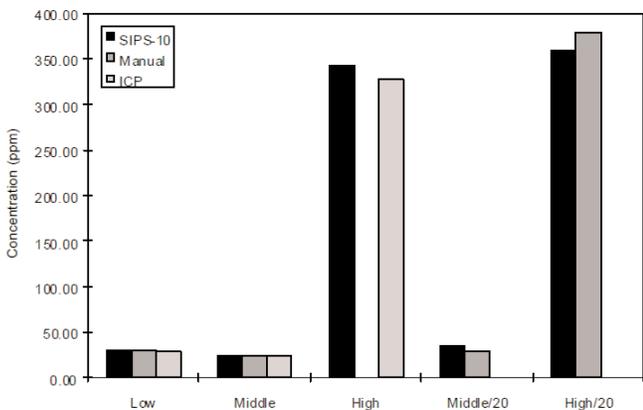


Figure 4. Comparison of the concentrations measured by various techniques of potassium in solid sodium chloride. The manual result for sample "High" was over-range and is not shown.

## Conclusion

The results for the manually diluted brine solutions and the solutions measured using SIPS compare very well. The SIPS system achieves the accuracy and reproducibility of manual dilutions. Even better results can be obtained by lowering the precision parameter from the default 1% value and increasing the default read time.

The Agilent SIPS therefore offers a routine laboratory significant savings in time and materials by eliminating manual tasks such as multiple standard preparation, and dilution and re-analysis of over-range samples. The on-line dilution capability of the SIPS also simplifies operation and reduces the risk of contamination.

An important advantage of the ICP-AES technique has been its linearity over a wide dynamic range, typically up to concentrations of  $10^4$ – $10^5$  times the detection limit. In many applications calibration with only one standard is required and sample dilution is often not required. The SIPS accessory now gives flame AAS similar benefits.

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