application note

Direct Determination of Trace Impurities in 30% NaCl and 40% $FeCl_3$ Solutions by ICP-OES

Introduction

The determination of elements in brines has been an important analysis in industry for many years. Brines are used in the production of many products such as sodium, magnesium, chlorine and chlorinated compounds. As trace impurities present in the brines can directly affect the efficiency and safety of these production processes, it is important to know the concentration of the constituents of the raw material.

When used for their electrolytic properties, brines also play an important role in electrode technology and related applications. In the development of water purification plants for example, quality control of brine purity is critical as impurities lead to ineffectiveness and corrosion of expensive electrodes.

Traditionally, the determination of impurities in brines by ICP-OES has presented many problems. The very high dissolved salt content (greater than 30% w/v) results in rapid salt build up in the nebulizer and torch components. Analysts have tried a number of methods to minimize salt build up including diluting the samples to 10% w/v to reduce the salt loading and switching to V-groove or Babington nebulizers that have a greater tolerance of high dissolved salts. However, switching to a V-groove nebulizer will not eliminate this dilution step and will further reduce the sensitivity of the application. Further, the dilution of critical elements of interest, such as Pb or Ni may mean that these elements will not be present in concentrations measurable by ICP-OES. These elements will require an alternative technique, such as Graphite Furnace Atomic Absorption (GFAA) for determinations.

This report describes the analysis of trace elements in 30% w/v brine and 40% $FeCl_3$ solutions by ICP-OES using a high precision concentric nebulizer to directly aspirate the undiluted sample. This approach results in the capability to reach new levels of detection for the analysis of trace impurities in these high salt sample types by ICP-OES.

GBC

Experimental

A GBC Integra ICP-OES was used for the analysis of the 30% NaCl solutions and 40% $FeCl_3$ solutions. A spectrometer fitted with the optional 1800 groove/mm holographic grating was employed. This provided typical resolution of 0.018 nm in 1st order, 0.009 nm in 2nd order, 0.007 nm in 3rd order and 0.006 nm in 4th order.

The Integra has Mass Flow Sensors fitted to the sample, plasma and auxiliary gas lines. Having the Mass Flow Sensor fitted to the sample gas provides a further advantage in the analysis of samples with high dissolved salt contents. It provides direct continuous monitoring of the nebulizer pressure, essential for the immediate diagnosis of nebulizer blockages. This parameter was monitored continuously throughout the duration of the analysis conducted for this report.

The standard set of sample introduction components was used. This included the high precision glass concentric nebulizer, low volume rapid wash cyclonic spraychamber and unique three piece demountable torch.

This report will focus on the analysis of the difficult elements Cd, Co, Cr, Cu, Ni, Pb and Zn which are present at very low levels. However other elements such as Ba, Sr and Ca which are present in higher concentrations can be measured using the method presented in this report.

The power, viewing height and sample gas flows were optimized to obtain the best signal-to-background ratio (SBR) using the unique Auto Optimization Simplex Algorithm.

Table 1: Instrument Operating Parameters used

Power (w)	1400
Plasma Gas (L/min)	12.00
Auxiliary Gas (L/min)	0.70
Sample gas (L/min) Sample gas (kPa)	0.60 301
Torch height (mm)	9.0
Pump speed (mL/min) Pump speed (rpm)	1.2 15
PMT (v)	600
Scan Window	0.08 nm 1st order 0.04 nm 2nd order 0.027 nm 3rd order 0.02 nm 4th order
Data Points	40
Integration Time Per Point(s)	0.5
On Peak Integration Time (s)	2
Replicates	3
Background Correction Mode	Dynamic
Fast pump between samples (s)	15
Stabilization time (s)	20
Rinse time (1% HNO3) (s)	20
Humidifier	ON

Sample and Standard Preparation

30% NaCl Sample Preparation

The 30% w/v NaCl was prepared by accurately weighing 300 g of analytical grade NaCl and quantitatively transferring this to a 1000 mL volumetric flask. Approximately 500 mL of distilled/deionised water was added and the flask was inverted to allow the NaCl to dissolve.

10 mL of concentrated HNO_3 was added to preserve the solution and also to stabilize the cations added in the standard preparation. This was then made to volume with high purity distilled/deionised water. The 15, 20 and 25 %w/v NaCl solutions were prepared as above except 150, 200 and 250 g of NaCl were weighed into respective volumetric flasks.

Standard Preparation

All standards were prepared from high purity 1000 ppm stock standard solutions acidified by the supplier with 0.5 M HNO_3.

30% NaCl

1) Working Standards
The working standards were made up to volume with the 30% NaCl as prepared in the sample preparation, in order to ensure matrix matching of the standards to the samples. The 30% NaCl solution was used for the calibration blank.

The selected wavelengths and concentrations of the standards are presented in Table 2. Note that for the 30% NaCl analysis all the calibration concentrations are ppb.

Table 2: The wavelengths and concentrations used for the analysis of 30% NaCl

Wavelength (nm)	Blank (ppb)	Standard 1 (ppb)
Cr 267.716	0	10.00
Mo 202.030	0	10.00
Ni 231.604	0	20.00
Pb 220.353	0	40.00
V 309.311	0	10.00

Wavelength (nm)	Standard 2 (ppb)	Standard 3 (ppb)
Cr 267.716	20.00	30.00
Mo 202.030	20.00	30.00
Ni 231.604	40.00	60.00
Pb 220.353	80.00	
V 309.311	20.00	40.00

15%, 20%, 25% and 30 % NaCl long term stability
The 15%, 20%, 25% and 30% w/v NaCl solutions were spiked with Ni to produce 0.8, 0.6, 0.4 and 0.2 ppm final Ni concentrations respectively.

40% $FeCl_3$ long term stability
The 40% w/v $FeCl_3$ was prepared by accurately weighing 400 g of analytical grade $FeCl_3$ and quantitatively transferring this to a 1000 mL volumetric flask. Approximately 500 mL of distilled/deionised water was added and the flask was inverted to allow the $FeCl_3$ to dissolve. 10 mL of concentrated HNO_3 was added to preserve the solution and also to stabilize the cations added in the standard preparation. This was then made to volume with high purity distilled/deionised water.

Results and Discussion

Long Term Stability

i) 15, 20, 25 and 30% w/v NaCl solutions
The reproducibility of signal measurement over time was measured as a function of NaCl concentration. This was achieved through repeated measurement of the Ni 231.604 wavelength for over two hours. The reproducibility plots are shown in Figure 1.

Table 3 summarizes the reproducibility achieving better than 2% RSD over the two hour period for all the measurements.

Table 3: Long term stability for various concentrations of NaCl measured using the Ni 231.604 nm line

Salt Concentration (%w/V)	%RSD for over 2 hr measurement
15	0.83
20	1.02
25	1.20
30	1.30

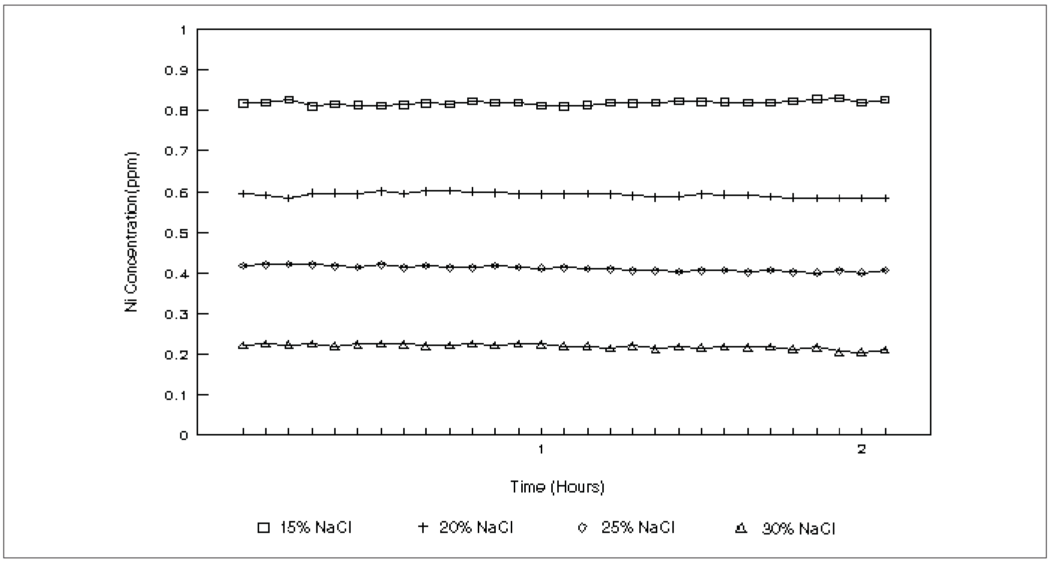


Figure 1 *Long term stability for 15%, 20%, 25% and 30% w/v NaCl using the Ni 231.604 nm line*

ii) 40% $FeCl_3$ solution

Figure 2 shows the reproducibility plots for six different elements in a 40%w/v $FeCl_3$ solution over a two hour period. Typically better than 4% RSD was achieved on this very difficult matrix for each element as summarized in Table 4. This is indicative of Integra's outstanding high dissolved salts capability.

Table 4: Long term stability for various elements in 40% $FeCl_3$

Element	%RSD for over 2 hr measurement
Cd 228.802	3.7
Co 228.616	3.0
Cr 205.552	3.8
Cu 327.396	3.6
Pb 220.353	3.7
Zn 213.856	3.9

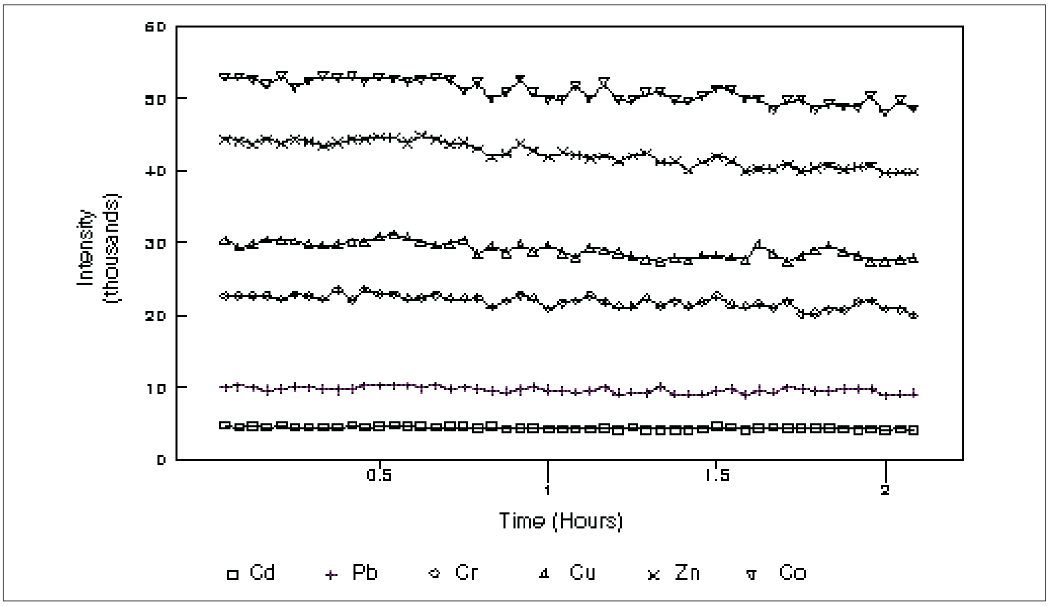
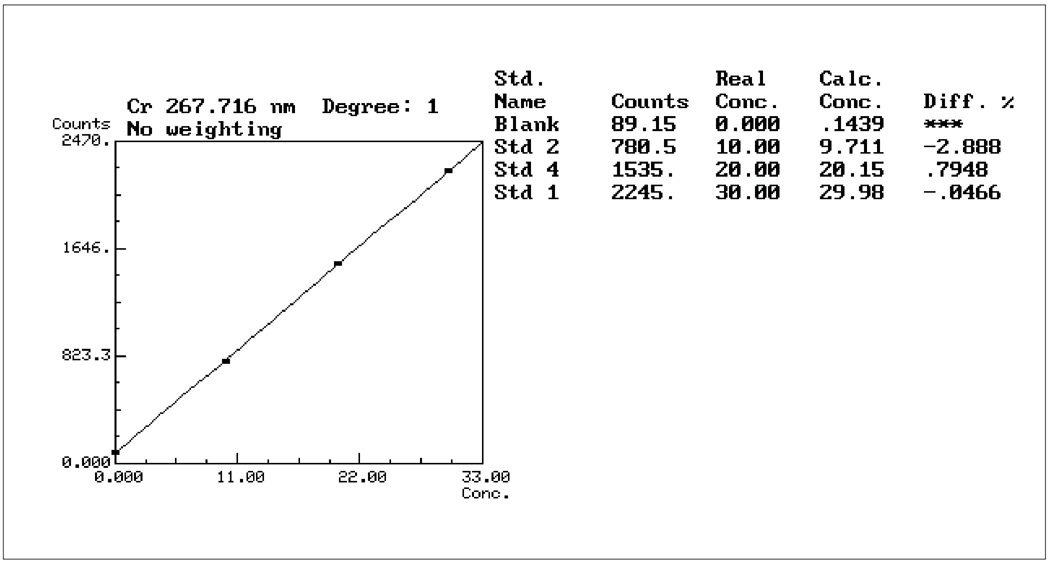


Figure 2 *Long term stability test for Cd, Cr, Pb, Cu, Zn and Co in 40% $FeCl_3$*

Reaching New Levels of Detection

Calibration graphs are shown for elements analysed in 30% NaCl in Figures 3–7. Note the excellent curve fits even at the low ppb concentrations and also in the difficult matrix analysed. The curve fit is defined by the 'calculated' and 'real' concentrations displayed with the calibration graphs. This linear curve fit was typically better than 1%.

The results of these curve fits provide excellent indicators to the capability of the Integra ICP to reach the lowest detection levels with detection to low ppb levels possible by ICP.



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Cr 267.716 nm   Degree: 1
No weighting

Std.                  Real     Calc.
Name      Counts      Conc.    Conc.    Diff. %
Blank     89.15       0.000    .1439    ***
Std 2     780.5       10.00    9.711    -2.888
Std 4     1535.       20.00    20.15    .7948
Std 1     2245.       30.00    29.98    -.0466
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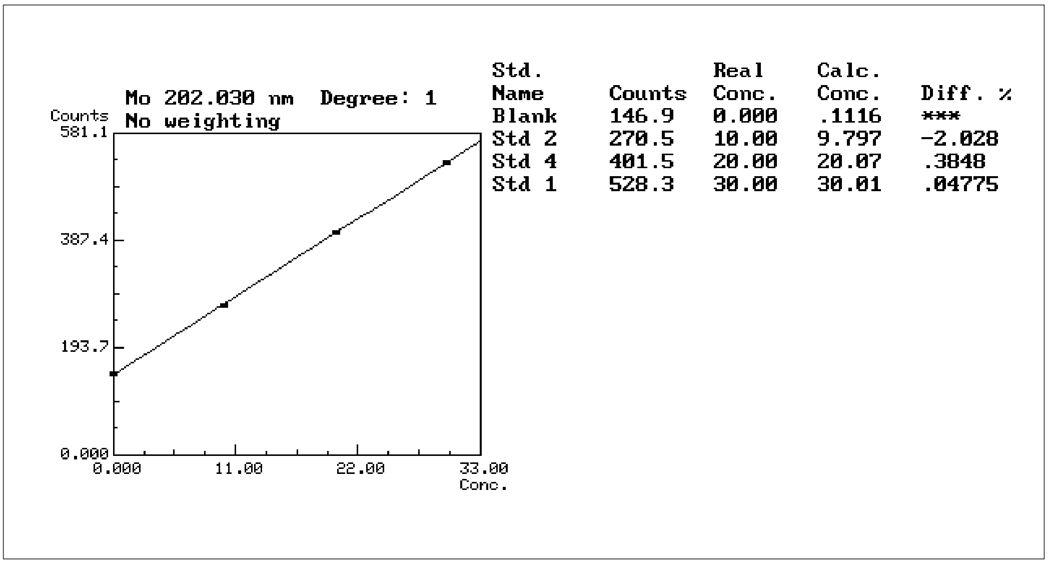
Figure 3 *Calibration up to 30 ppb Cr in 30% NaCl using the Cr 267.716 nm line*



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Mo 202.030 nm   Degree: 1
No weighting

Std.                  Real     Calc.
Name      Counts      Conc.    Conc.    Diff. %
Blank     146.9       0.000    .1116    ***
Std 2     270.5       10.00    9.797    -2.028
Std 4     401.5       20.00    20.07    .3848
Std 1     528.3       30.00    30.01    .04775
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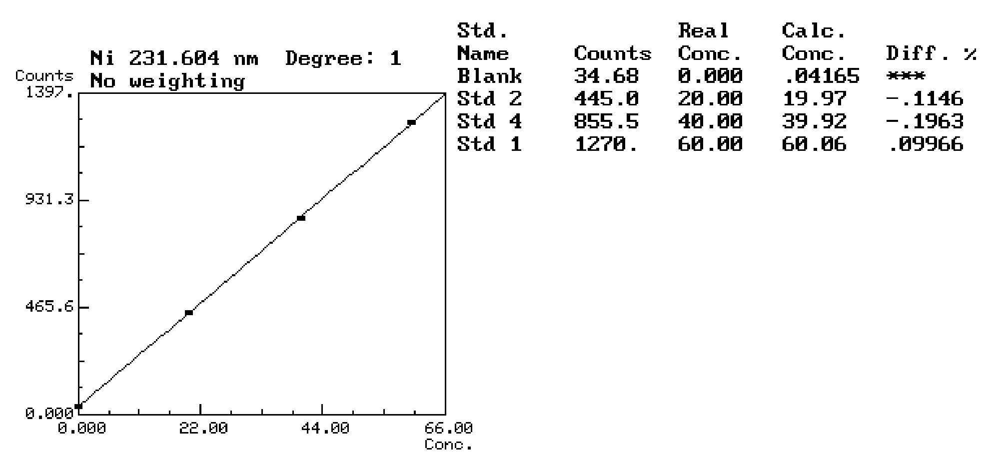
Figure 4 *Calibration up to 30 ppb Mo in 30% NaCl using the Mo 202.030 nm line*



```
Ni 231.604 nm   Degree: 1
No weighting

Std.                  Real     Calc.
Name      Counts      Conc.    Conc.    Diff. %
Blank     34.68       0.000    .04165   ***
Std 2     445.0       20.00    19.97    -.1146
Std 4     855.5       40.00    39.92    -.1963
Std 1     1270.       60.00    60.06    .09966
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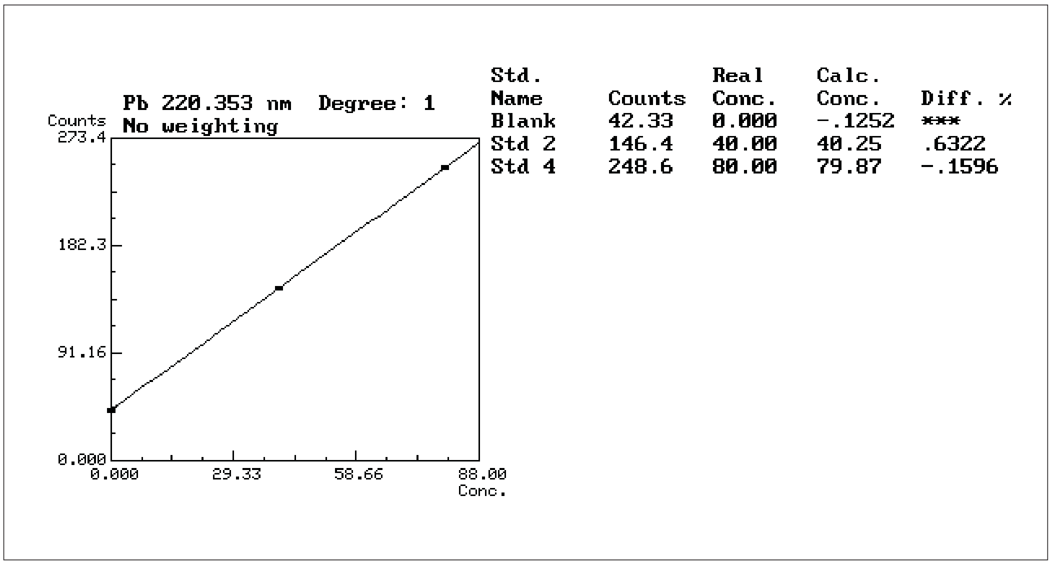
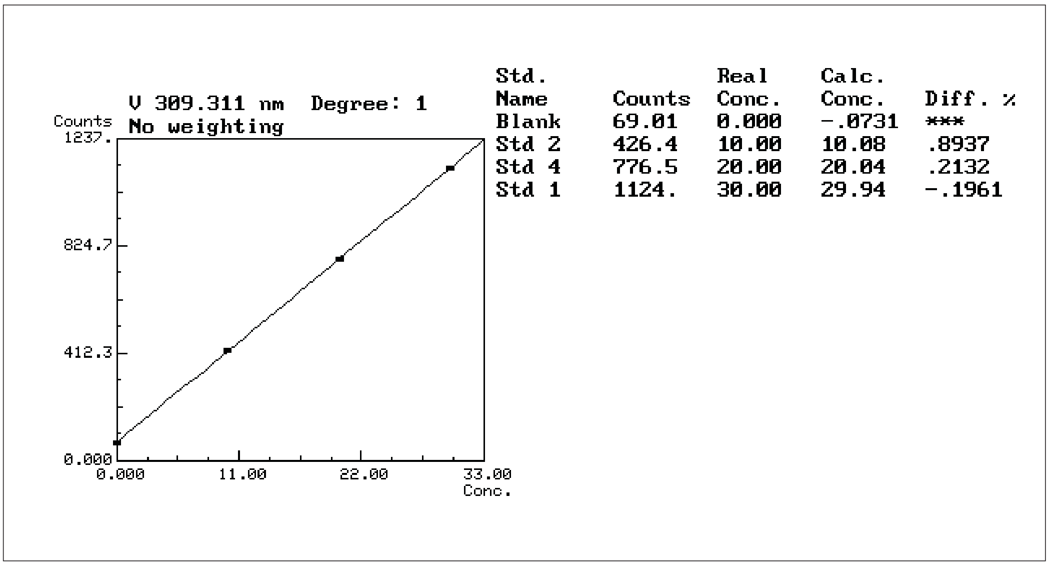
Figure 5 *Calibration up to 60 ppb Ni in 30% NaCl using the Ni 231.684 nm line*



```
Std.                Real     Calc.
Name      Counts    Conc.    Conc.    Diff. %
Blank     42.33     0.000    -.1252   ***
Std 2     146.4     40.00    40.25    .6322
Std 4     248.6     80.00    79.87    -.1596
```

Figure 6 *Calibration up to 80 ppb Pb in 30% NaCl using the Pb 220.353 nm line*



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Std.                Real     Calc.
Name      Counts    Conc.    Conc.    Diff. %
Blank     69.01     0.000    -.0731   ***
Std 2     426.4     10.00    10.08    .8937
Std 4     776.5     20.00    20.04    .2132
Std 1     1124.     30.00    29.94    -.1961
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Figure 7 *Calibration up to 30 ppb V in 30% NaCl using the V 309.311 nm line*

Conclusion

The Integra ICP offers unique capabilities that overcome the traditional limitations presented by the analysis of trace impurities in solutions with high dissolved salt concentrations. The GBC Integra provides the capability to perform direct determination on the toughest matrices such as 30% NaCl or 40% $FeCl_3$ solutions for extended periods without blockage of the sample introduction components.

In summary the direct aspiration of these traditionally difficult samples provides distinct advantages to the analyst including the following:

- The elimination of time consuming dilutions which add to the sample preparation time,
- The elimination of dilution errors,
- The elimination of the risk of introducing contaminants in the dilution step, and
- The sensitivity of the application is enhanced since the analyte levels are not diluted.

Using a high precision concentric nebulizer and eliminating time consuming dilution steps, the GBC Integra offers the lowest detection limits possible in the toughest samples and hence allows the ability to reach new levels of detection.

References

1. Montaser, A. and Golightly D.W. Analytical Performance of Inductively Coupled Plasma—Atomic Emission Spectrometry, Inductively Coupled Plasmas in Analytical Atomic Spectrometry, Second Edition, VCH Publishers Inc. New York, 1992, Chapter 5, pages 279–281.

2. GBC Integra Operation ICP-OES Methods Manual.

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