# Optimization and Calibration of the J-A Model 975 Plasma Atomcomp Spectrophotometer

T.C. Waugh and L.R. Hathaway
Analytical Services
Kansas Geological Survey

## Introduction

The general set-up of the Inductively Coupled Argon Plasma (ICAP) as outlined in the operational manual should be observed.(1) However, several additional stages of adjustment of components in the torch cabinet of the ICAP must be completed before optimum performance of the plasma can be expected in the determination of quantitative data for aqueous samples. Alignment of the work coil usually is only required at the initial setup of the instrument, but will be necessary if the coil is accidently moved or must be replaced. More common are the optimization steps which accompany the replacement of the quartz torch. Variability in the dimensions and operational characteristics of the torches necessitate a check of location of the torch tip with respect to the work coil,(2) the determination of proper mass flow controller settings for the Argon (Ar) gas supplies,(2) the determination of the peristaltic pump rate for sample uptake,(3) the optimization of the viewing optics for both the polychromator and monochromator, and the establishment of calibration curves for calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K) following torch replacement.

The height of the innermost torch tip with respect to the work coil must be such that the aspirated sample will puncture the toroid of the plasma, but not so high that it will be destroyed by the heat of the plasma.(2) Also, changes in signal stability and the effects of ionization-buffering may be noted if the exchange of torches results in a change of the thermal conditions of the zone of the plasma being viewed by the polychromator and the monochromator; the alkali metals Na and K are especially notorious in this regard.(3) The sequential steps for the optimization of components in the torch cabinet of the ICAP are detailed in the following sections.

## Positioning of the Work Coil

The first step in the optimization of the torch cabinet components is the vertical positioning of the work coil such that the nominal viewing height in the plasma, about 16 mm above the work coil, will fall in the mid-operating range of the vertical mirror micrometer which is associated with the polychromator viewing optics. Proper location of the work coil is facilitated by the use of an Alignment Tool which has been constructed from a thin aluminum plate, Figure 1. The narrow center tab of the tool is placed between the work coil and the torch and the two horizontal stops are allowed to rest on the top of the coil. This places the tip of the index slot at a distance of 16mm above the top of the coil. The room is darkened, the tool is illuminated by a light source through the front door of the cabinet and the image of the index slot of the tool is observed on the viewing screen at the front of the cabinet.

The vertical mirror micrometer for the polychromator is turned to bring the image of the index slot to its lowest possible position. A wax pencil is used to mark the top of the index image on the viewing screen. The micrometer is then turned to bring the index image to its highest possible position, and the top of the index image is marked on the viewing screen. The micrometer is finally adjusted so that the top of the index image is at a point midway between the two wax pencil marks. At this point the top of the index slot image should be within ±2mm of the cross-hairs of the viewing screen.

If the top of the index slot image is not within ±2mm of the cross-hairs, carefully bend the leads of the work coil to bring the top of the index image within acceptable limits. Care must be taken to maintain the concentricity of the work coil about the torch during this adjustment process.

Once the vertical position of the work coil has been established it should not be necessary to repeat this process as subsequent torch changes are made. However, re-optimization should begin with this process of the coil is moved or replaced.

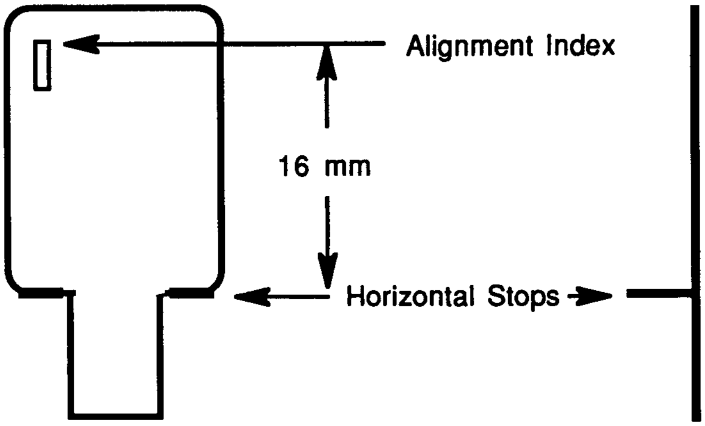

Figure 1. Front and side view of Alignment Tool for establishment of proper vertical location of the work coil.

## Torch Installation

The torch is positioned on top of the vertical exit of the spray chamber and is secured to the spray chamber by means of a clamp which fits around the ball-joint connection. The vertical height of the torch should place the innermost tip about 4 to 5mm below the bottom of the work coil. Vertical adjustment of the torch is made by loosening the four screws on the bracket which supports the spray chamber and sliding the torch up or down with respect to the work coil. Once positioned correctly, the four screws are tightened. If the torch is not centered within the work coil, the two thumb screws which secure the spray chamber are loosened. The chamber is rotated or moved in or out to properly space the torch laterally within the work coil. Centering of the torch within the work coil assures an even cooling of the torch by the coolant Ar gas supply.

If the torch becomes dirty, it should be removed, cleaned in Aqua Regia, rinsed with distilled water, dried and re-installed. This cleaning process does not necessitate the redetermination of the mass flow controller settings, optimal viewing heights or calibration curves such as would be required with torch replacement. Peaking of the plasma with a dilute cadmium (Cd) solution and adjustment of the horizontal mirror micrometer should re-establish optimal operating conditions for the ICAP.

## Mass Flow Controller Settings

Two mass flow controller units are employed with the ICAP. One unit controls the coolant Ar gas supply, while the other unit regulates the sample Ar gas supply.(2) The mass flow controller for the coolant argon gas supply is adjusted so that the ball flowmeter on the front panel of the ICAP gives a reading of 20 Lpm. The settings employed for the mass flow controller for the sample argon gas supply must be determined each time a new torch is installed in the ICAP. To determine this setting, a 1000 ppm yttrium (Y) solution is aspirated and the mass flow controller is adjusted until a red tongue is visible in the plasma about 2 to 3mm above the work coil. It is important that the red tongue does not extend beyond this range; otherwise a noticeable reduction in signal stability may be experienced in the viewing zone about 16mm above the work coil.

Small variations in the coolant gas supply seem to have little if any effect upon the sensitivity and optimization of the ICAP; whereas such variations in the sample gas supply have a marked impact upon the response of the ICAP in quantitative analyses.(3) The purity of the Ar gas can have a marked effect upon the operation of the mass flow controllers. Changes in the responses of the ball flowmeters following a switch of Ar gas cylinders, or a change in suppliers of gas products, may signal changes in the purity of the Ar gas. The mass flow controller for the coolant gas supply can be adjusted to bring the flowmeter to the 20 Lpm level; but the Y-solution should be used to check and adjust the setting of the mass flow controller for the sample gas supply. If the sample Ar gas port in the nebulizer becomes partially blocked in the course of an analytical run the ball of the flowmeter for the sample gas supply may fall to a lower position. Under this condition of partial blockage the mass flow controller will cause the velocity of the gas entering the nebulizer to be higher than normal and the thermal state of the viewing zone of the plasma will not be that upon which the system was optimized. The nebulizer should be cleaned with an RBS solution in a small ultrasonic bath, rinsed, and reinstalled on the open end of the spray chamber. After cleaning, the flowmeter for the sample gas supply should return to its former position and the optimal viewing zone should be re-established.

## Peristaltic Pump Rate

The normal unpumped aspiration rate of the nebulization-torch system is determined by observing the uptake rate of solution from a 10ml graduated cylinder per unit time. This unpumped rate generally is in the range of 0.5 to 1.0 ml/min. The peristaltic pump is then adjusted to deliver 3 times the normal volume per minute. This over pumping of the normal aspiration rate serves to wash out the nebulization chamber and seems to improve the stability of signals from the alkali metals. A baffle has been inserted into the rear one-third of the spray chamber to help reduce the number of larger droplets reaching the plasma and thus improve the signal stability.

## Determination of Optimum Viewing Height for the Polychromator

The polychromator of the ICAP is configured to measure the intensities of both atom and ion lines. Thus, it is important to establish a viewing zone in the plasma where the response of both atom and ion line intensities are independent of changes in the matrix composition, a zone where effects such as ionization buffering and quenching which plague AA–OES are minimized. This zone will be about 16mm above the work coil, but will vary from torch to torch, and must be determined experimentally for each new torch as it is installed in the ICAP.

Three standardization solutions are used to evaluate the optimum viewing height for a given torch. These solutions are 100ppm Ca, 100ppm Na, and 100ppm Ca and Na. Sodium is determined using an atom line (5890Å) and Calcium is determined using an ion line (3968Å); thus these three solutions make it possible to monitor the independence of the atom and ion lines as a function of viewing height in the plasma. Typically the range of 12 to 22mm above the work coil is evaluated in 1mm incremental steps.

The evaluation process is begun at the minimum height setting, 12 mm above the work coil, by adjustment of the vertical mirror micrometer. A mercury line profile is performed in order to bring each spectral line onto its respective photomultiplier slit. Next the Profile Command is set to read the Physical Channel 21 (Cd) and a dilute Cd solution is aspirated. The Cd signal is peaked by adjusting the horizontal mirror micrometer. The ICAP is then standardized using distilled water as the blank and the 100ppm Ca and Na solution as the upper standard. Throughout the process of viewing height evaluation two burn sequences of triplicate 12-second exposures are used for each solution. After standardization the following solutions are run: (1.) 100ppm Ca and Na (to confirm the standardization, (2.) 100ppm Ca, (3.) 100ppm Na, and (4.) 100ppm Ca and Na (to check instrument drift). If the data are acceptable, the offsets and gains are printed out. The vertical mirror micrometer is advanced to the next step and the entire process is repeated until the total vertical range of interest has been examined.

The data from the incremental steps are examined to find the range of heights over which the 100ppm Ca and 100ppm Na solutions yield the same reported concentrations as obtained from the 100ppm Ca and Na solution. The gains are then examined for Ca and Na at the heights which appear independent of matrix change and a viewing height is selected which is midpoint both in the constant concentration response range and in the range of similar gain values.

## Determination of the Optimum Viewing Height for the (N+1) Channel Monochromator

The (N+1) Channel is used for the determination of K in the analysis of natural waters. Potassium, like Na, is an alkali metal element and its determination is based upon the measurement of intensity of an atom line. Therefore, Na is used to optimize the viewing height of the monochromator because the Na channel of the polychromator can be used to monitor the Na signal during the optimization process and also because the Na line (5890Å) exhibits a greater sensitivity than the K line (7665Å).

The wavelength of the monochromator for the (N+1) channel is peaked at the 5890Å Na atom line. The uppermost micrometer on the mirror support controls vertical adjustments for the viewing zone of the monochromator. Micrometer settings over the range of 140 to 280 units are evaluated using a step interval of 20 units. The vertical adjustment micrometer is set to a reading of 140 units to begin the evaluation process. A 2 to 3 ppm Na solution is aspirated, the Profile Command is set to read Physical Channel 27 (N+1), and the signal is peaked by adjusting the horizontal mirror micrometer of the monochromator optical system. The ICAP is then standardized using distilled water as the blank and the 100 ppm Ca and Na solution as the upper standard. After standardization the following solutions are run: (1.) 100ppm Ca and Na (check on standardization), (2.) 100ppm Na, and (3.) 100ppm Ca and Na (check of instrument drift). Again, two burn sequences of triplicate 12-second exposures are used for each solution. Na in the polychromator is monitored for each step as a check on signal stability during the burn sequences. If the data are acceptable, the offsets and gains are printed out. The vertical adjustment micrometer is moved up 20 units and the entire process of signal peaking, standardization, and Na measurement of the test solutions is repeated until the total vertical range of interest has been examined.

The data from the incremental steps are examined to find the range of micrometer settings over which the Na concentration data from the (N+1) monochromator are the same for the 100ppm Ca and Na and the 100ppm Na solutions. The gains for this range of settings are examined for similarity, and a setting is selected for the vertical adjustment micrometer which is mid-range for both constant concentration response and similarity of gain value. Experimentally determined values of the micrometer setting have been about 200 units. After optimization, the monochromator wavelength is peaked at 7665Å for K.

## Calibration for major Constituents of Natural Waters ($SiO_2$, Ca, Mg, Na, and K)

The ICAP has been viewed as being free of chemical and ionization interferences which tend to trouble AA and AA-OES analyses because of the higher temperatures encountered in the plasma. Spectral interferences are recognized to still present problems in elemental analyses. Concentration vs. intensity responses are reported to be linear over several decades of concentration. The instrument manufacturer recommends a two point calibration of all species to be determined by the ICAP; this involves a 0ppm blank solution (distilled water) and a solution which is 10ppm in each species of interest.(1) A "mathematical curve" is generated within the ICAP which extends from 0ppm through 10ppm and is extrapolated upward for higher concentrations. Major components of natural water which are determined using the ICAP often exhibit concentrations in excess of 10ppm, even in solutions diluted to bring the total dissolved solids level to about 1000ppm. It is poor practice in quantitative analyses to have the determined value of the unknown solution fall outside the range of the standards of the calibration curve. In the case of the ICAP calibration, slight fluctuations in the the measured intensities of the blank or 10ppm standard can adversely affect the slope of the calibration curve and introduce unknown uncertainties into determined concentrations above the 10ppm level if the calibration curves are not truly linear over the range of the determinations. Experimental work with the optimized ICAP system has shown that the curves for Ca and Na are not truly linear over the 0 to 100ppm range and that curve correction improves the Mg and K data over the 0 to 20ppm range. Silicon (Si), reported as $SiO_2$, has been found to be linear over the range of 0 to 21ppm.

In the analysis of natural water samples the concentrations of Ca and Na are held to levels under the 100ppm in the solution analyzed. The concentrations of Mg and K in these solutions will normally be less than 20ppm. The optimized ICAP is calibrated using a distilled water blank and an upper calibration standard which is 100ppm in Ca and Na, 20 ppm in Mg and K, and 21.39 ppm in $SiO_2$ (10ppm Si). The upper calibration standard is rerun after every three unknown samples as a control. The non–linearity of the Ca, Mg, Na, and K curves is addressed through experimentally determined calibration curve values which are incorporated in the "Group V" calibration curves of the of the Data Base Matrix.

The primary standard used for the preparation of calibration solutions is and XKGS-1 ICAP Standard solution manufactured by SPEX Industries which contains 1000ppm Ca and Na and 200ppm Mg and K. A 1-to-10 dilution of this standard produces a calibration solution which is 100ppm in Ca and Na, and 20ppm in Mg and K. The 1-to-10 dilution is then used to prepare the following calibration solutions: (1.) 90ppm in Ca and Na, 18ppm in Mg and K; (2.) 75ppm in Ca and Na, 15ppm in Mg and K; (3.) 50ppm in Ca and Na, 10ppm in Mg and K; (4.) 25ppm in Ca and Na, 5ppm in Mg and K; and (5.) 10ppm in Ca and Na, 2ppm in Mg and K. After standardization of the ICAP with the blank and the upper calibration standard (100ppm Ca and Na, 20ppm Mg and K), the upper calibration standard and the other five calibration solutions are run as samples. Two burn sequences of triplicate 12-second exposures are used for each solution. Composite averages of uncorrected concentration data ("B" mode) are then entered together with the true concentration values into the Data Base Matrix, Group V (Curve Calibration), see Table 1.

## Summary

The vertical positioning of the work coil should be checked following installation of the ICAP unit. A recheck of the work coil position is not required following replacement of the torch. However, accidental movement or replacement of the coil would necessitate a check of its positioning as will as rechecks of the torch placement within the coil, mass flow controller setting for the sample gas supply, optimum viewing heights for the monochromator and polychromator, and calibration curves loaded into Group V of the Data Base Matrix.

Torch replacement must be accompanied by the following sequential steps: (1.) positioning of the torch both vertically and laterally within the work coil, (2.) setting of the mass flow controllers for coolant and sample argon gas supplies, (3.) determination of the proper peristaltic pump rate, (4.) optimization of the viewing height for both the polychromator and the monochromator optical systems, and (5.) establishment of calibration curves for Ca, Mg, Na, and K. Cleaning of the torch or nebulizer usually does not require a complete re-optimization and recalibration of the ICAP before quantitative analyses can be resumed. Normally a peaking of the plasma by adjustment of the horizontal polychromator and monochromator mirror micrometers is sufficient to re-establish optimum operational conditions following cleaning of the torch, and a check with a Y-solution following the cleaning of the nebulizer will determine if the sample gas supply is being introduced at the proper rate.

Changes in the purity of the Argon gas, which may occur with a change in vendor, can adversely affect the response of the mass flow controllers. A Y-solution can be used to determine if the mass flow controllers are properly set when a gas supply from a new source is put into service.

Lastly, plasma grade standards, rather than AA standards, should be used in the calibration and standardization of the ICAP. The purity of AA standards often is not sufficient to allow consistent quality in quantitative analyses by the ICAP.

## TABLE 1

# Example of Group V Curve Calibration Data

| | |
|---|---|
| CURVE NAME: SIO2 | |
| 1000.00 | 1000.00 |
| 0 | 0 |
| CURVE NAME:CALC | |
| 119.999 | 119.999 |
| 100.019 | 100.019 |
| 90.9375 | 90.0000 |
| 76.8164 | 75.0000 |
| 52.9394 | 50.0097 |
| 27.3046 | 24.9902 |
| 11.2500 | 9.99023 |
| 0 | 0 |
| CURVE NAME:MAGS | |
| 25.0000 | 25.0000 |
| 20.0012 | 20.0012 |
| 18.0541 | 17.9992 |
| 15.0390 | 15.0024 |
| 10.1318 | 9.99755 |
| 5.11474 | 4.99877 |
| 2.02636 | 1.99584 |
| 0 | 0 |
| CURVE NAME:NACL | |
| 119.999 | 119.999 |
| 100.019 | 100.019 |
| 90.2636 | 90.0000 |
| 75.2343 | 75.0000 |
| 50.9765 | 50.0097 |
| 25.7812 | 24.9902 |
| 10.3710 | 9.99023 |
| 0 | 0 |
| CURVE NAME:POTS | |
| 25.0000 | 25.0000 |
| 20.0012 | 20.0012 |
| 17.9931 | 17.9992 |
| 15.0024 | 15.0024 |
| 10.0402 | 9.99755 |
| 5.10864 | 4.99877 |
| 2.03247 | 1.99584 |
| 0 | 0 |
| CURVE NAME:TRCE | |
| 10.0000 | 10000.0 |
| 0 | 0 |

(1) The Inductively Coupled Argon Plasma AtomComp, no date, Jarrell-Ash Div./Fisher Scientific, Waltham, MA, Cat. No. 96-975, 47p.

(2) Greenfield, S., 1987, Common Radio Frequency Generators, Torches, and Sample Introduction Systems: in Inductively Coupled Plasmas in Analytical Atomic Spectrometry, Montaser, A. and Golightly, D.W., (ed.), VCH Publishers, Inc., New York, pp. 123-161

(3) Thompson, M., 1987, Analytical Performance of Inductively Coupled Plasma-Atomic Emission Spectrometry: in Inductively Coupled Plasmas in Analytical Atomic Spectrometry, Montaser, A. and Golightly, D.W., (ed.), VCH Publishers, Inc., New York, pp. 163-199