

Myers - Tracy Signal Compensation in Inductively Coupled Plasma Atomic Emission Spectrometry With High Dissolved Solids Solutions*

John Marshall, Gerard Rodgers† and William C. Campbell

Materials Analysis and Testing Group, Wilton Materials Centre, ICI plc, Middlesbrough TS6 8JE, UK

A preliminary study has been made of the use of Myers - Tracy signal compensation in inductively coupled plasma atomic emission spectrometry (ICP-AES). It was found that significant improvements in precision, in some instances up to ten-fold, could be obtained in comparison with normal ICP-AES operation. Matrix effects caused by the presence of up to 10% *m/V* potassium chloride were reduced by the use of signal compensation. However, deviations from standard plasma conditions are required to optimise the effect of ratioing to the internal standard. A comparison of the performance of a high dissolved solids nebuliser and a cross-flow nebuliser showed that the former provides better precision in a potassium chloride matrix in the determination of manganese and copper. Nevertheless, Myers - Tracy signal compensation was found to improve the precision performance of both nebulisers.

Keywords: *Inductively coupled plasma atomic emission spectrometry; Myers - Tracy signal compensation; internal standardisation; nebuliser*

The general recognition of matrix effects in inductively coupled plasma atomic emission spectrometry (ICP-AES) has led to a resurgence of interest in internal standardisation.¹⁻¹⁵ The procedure relies on the addition of one or more elements to the samples and standards in order to correct for variations in the analyte response arising from the adverse effects associated with the constituents in the sample matrix, or from instrumental factors. It is clear that this procedure will be most effective if the behavioural characteristics of the internal standard and the analyte elements are very similar with respect to the plasma conditions and interference effects.^{2,13} In simultaneous multi-element ICP-AES, the use of an internal standardisation procedure is attractive, as a number of spectrometer channels can be made available for reference measurements. However, there is some difficulty in electing an internal standard that will be suitable in the measurement of a wide range of analytes. Thus methods have been proposed which can be employed to identify and correct for multi-element correlated variance by using multiple internal standards.⁵⁻⁷

There is also a need for internal standardisation in sequential multi-element ICP-AES using a slew-scanning monochromator. However, the normal mode of measurement precludes simultaneous monitoring of the analyte and the internal standard signals. It is possible to obviate this limitation by employing a second monochromator to monitor the internal standard emission intensity.^{6,10} Dual-channel instruments are used in routine analytical determinations primarily to increase the rapidity of sequential measurement, and consequently, sample throughput. The dedication of one channel of such an instrument to provide what is essentially a reference signal, is a relatively expensive approach to the problem. Further, the selection of an appropriate or "compromise" element as a single internal standard is still a considerable difficulty.^{4,5} Myers and Tracy⁶ have demonstrated using a dual monochromator system, that it is possible to use a single internal standard with suitable ICP conditions to achieve substantial improvements (up to 20×) in the noise characteris-

tics of analytical signals. It was concluded that very good control of both r.f. power and carrier gas flow-rate was required in order to maximise the effectiveness of the internal standardisation.

A commercial variant of the Myers - Tracy procedure has been incorporated in the design of the Perkin-Elmer Plasma II spectrometer. In this system, 5% of the incident radiation from the plasma is diverted using a beam splitter and passed to a signal compensation assembly, consisting of two filter photometers which monitor the argon (plasma background) and scandium (internal standard) line intensities, respectively. The advantages of the use of scandium as an internal standard are documented elsewhere,^{5,11} but there have been few publications which characterise the analytical performance of this particular configuration.⁵

Internal standardisation may be used to compensate for transport effects which result from variations in solution uptake rate, nebulisation efficiency, or solvent loading from sample to sample. Matrix matching of samples and standards may be used to ameliorate such effects, but this procedure does not take account of the specific variations which occur during the introduction of individual solutions. Often, the exact composition of the sample matrix is unknown, and consequently, matrix matching is not feasible. In such circumstances, the use of signal compensation to correct for the resultant differences in the response from samples and standards offers a means of improving accuracy and precision. The analysis of solutions containing relatively high levels of dissolved solids has been problematical in ICP-AES because of the difficulties in sample introduction, and in some instances, because of interference effects.¹⁴ It has been demonstrated that nebulisers based on the Babington design¹⁵⁻¹⁸ offer significant advantages in handling samples of this type.

In the present work, a study has been made of the use of Myers - Tracy signal compensation in the measurement of manganese and copper in synthetic solutions containing up to 10% *m/V* potassium chloride. The analytical performance of the system was assessed using both a Perkin-Elmer cross-flow nebuliser, and an Ebdon V-groove nebuliser.^{18,19}

Experimental

Instrumentation

A Perkin-Elmer Plasma II sequential ICP-AES system was employed for all measurements. Details of spectrometer

* This paper is dedicated to the memory of Professor John M. Ottaway. Two of the authors (J.M. and W.C.C.), are former Ph.D. students of John Ottaway and worked in close association with him over many years. We wish to acknowledge our gratitude to him as a supervisor, colleague, and friend. He is greatly missed.

† Present address: Department of Physics, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, UK.

Table 1. Operating parameters

<i>Spectrometer, Perkin-Elmer Plasma II—</i>			
Focal length	1.0 m
Reciprocal dispersion	0.527 nm mm ⁻¹
Resolution	0.018 nm
Photomultiplier gain	600 V
Peak window	0.025 nm
Search window	0.05 nm
Sampling time	100 ms
Wavelength:	Mn	..	257.610 nm
	Cu	..	324.754 nm
	Sc	..	424.683 nm
	Ar	..	419–420 nm
Filter band-pass	Sc	..	1 nm
	Ar	..	1 nm
(No interference by Mn or Cu observed)			
<i>Plasma—</i>			
Generator frequency	27.12 MHz
Generator power (maximum)	1.8 kW
Plasma gas flow-rate	15 l min ⁻¹
Auxiliary gas flow-rate	1.0 l min ⁻¹
Nebuliser gas flow-rate	1.0 l min ⁻¹
Solution pump-rate			
(a) Cross-flow nebuliser	1.0 ml min ⁻¹
(b) Ebdon nebuliser	2.0 ml min ⁻¹
Operating power	1000 W
Observation height	15 mm above load coil

parameters are given in Table 1. A demountable plasma torch unit²⁰ was used with a 2 mm-i.d. injector tube inserted. Two sample introduction systems were employed. A cross-flow nebuliser and associated double-pass spray chamber, both made of Ryton, were supplied by the manufacturer. In addition, an Ebdon¹⁸ V-groove high dissolved solids nebuliser was used. This nebuliser push-fitted directly on to the end of the Perkin-Elmer spray chamber. An adaptor was fitted to the nebuliser tubing to allow direct connection to the nebuliser gas supply. It was observed that pulsing occurred during the production of aerosol using the high dissolved solids nebuliser. This problem could be eliminated by increasing the solution flow-rate. Otherwise, the conditions used were exactly the same as those for the cross-flow nebuliser. The plasma was operated under the manufacturer's "standard operating conditions" which are the default conditions for general purpose analysis. These conditions are given in Table 1. All results reported are based on the mean of ten replicate measurements.

Reagents

Manganese and copper standard solutions were prepared freshly as required by serial dilution of 1000 µg ml⁻¹ stock solutions (BDH, Poole, Dorset, UK). A 1000 µg ml⁻¹ stock solution of scandium was prepared by dissolving the appropriate amount of scandium oxide (BDH, laboratory-reagent grade, 99.9%) in hydrochloric acid. AnalaR grade potassium chloride was used in the preparation of all interferent solutions (BDH). Distilled water was used as a diluent and blanks of all reagents were checked during the study for contamination.

Results and Discussion

The selection of a single internal standard inevitably results in a compromise in performance, if a number of elements are to be determined. Two emission lines (Mn II, 257.610 nm and Cu I, 324.754 nm) were selected as representative "hard" and "soft" lines, as categorised elsewhere.²¹ Calibration graphs were constructed for each of these elements and the coefficients of variation of the analyte responses were measured for

Table 2. Variation of precision obtained with respect to concentration in the determination of copper and manganese. Signal compensation was not used

Concentration of element/ µg ml ⁻¹	Coefficient of variation			
	Copper		Manganese	
	A*, %	B†, %	A*, %	B†, %
0.01	1.38	1.49	2.21	3.22
0.05	1.38	1.27	1.33	1.77
0.10	0.98	1.04	1.15	0.97
0.50	0.97	1.23	0.68	0.99
1.0	0.95	1.15	0.60	1.18
5.0	1.01	0.97	0.72	1.09
10	0.63	1.39	0.64	1.03
50	0.90	1.48	0.60	1.43
100	0.89	0.88	0.76	1.07

* Cross-flow nebuliser.
† Ebdon high dissolved solids nebuliser.

Table 3. Effect of scandium content on precision for the determination of 10 µg ml⁻¹ of manganese

Scandium content/µg ml ⁻¹	Internal standard ratio	Coefficient of variation, %
5	740	0.45
10	390	0.26
20	202	0.27
50	79	0.23

both nebulisers. As can be seen from Table 2, the precision data are relatively constant, except at low concentrations, for each element. Consequently, it was decided to select analyte concentrations of 10 µg ml⁻¹ of copper and manganese for interference studies.

It is of some importance when utilising an internal standard, to select an appropriate concentration level for the measurement. The effect of scandium content on the measured precision for a solution containing 10 µg ml⁻¹ of manganese as analyte, is shown in Table 3. An indication is given of the background-subtracted internal standard ratio measurement provided by the Myers-Tracy signal compensation procedure. The ratio values decrease in a linear manner with increasing scandium content. It would appear that there is little to be gained by adjusting the scandium concentration in the range 10–50 µg ml⁻¹. A concentration of 50 µg ml⁻¹ of scandium was employed for all subsequent work. No spectral interferences or contamination from the internal standard was observed when using this concentration.

An investigation was carried out to determine the effect of 0–10% m/V of potassium chloride on the emission intensity of the copper atom line at 324.754 nm. Distilled water was aspirated as a blank between each potassium chloride solution to avoid the cumulative build-up of the matrix. Interferent solutions were run in order of increasing salt content. Both nebulisers were employed in turn, and results were obtained with and without Myers-Tracy signal compensation (see Table 4). It can be seen from a comparison of the precision values obtained using each nebuliser without signal compensation that a superior performance is achieved using the high dissolved solids design, particularly at high salt concentrations. Using the cross-flow nebuliser, the precision appears to worsen gradually with increasing salt concentration, whereas for the high dissolved solids nebuliser, the precision achieved is relatively uniform with respect to the potassium chloride content. However, when signal compensation was employed, the coefficients of variation obtained for both nebulisers were significantly improved, and in many instances by as much as 5–10-fold. Indeed, the coefficients of variation for copper in the presence of 10% m/V potassium chloride are substantially less than 1%, which indicates that the signal compensation

Table 4. Effect of potassium chloride concentration on the determination of 10 µg ml⁻¹ of copper

KCl matrix, % m/V	Cross-flow nebuliser				Ebdon nebuliser			
	A*		B†		A*		B†	
	CV‡, %	Signal recovery, %	CV‡, %	Signal recovery, %	CV‡, %	Signal recovery, %	CV‡, %	Signal recovery, %
0.0	0.96	100	0.31	100	1.06	100	0.27	100
0.1	0.83	92	0.26	97	0.94	95	0.26	98
0.2	1.20	91	0.19	96	1.51	93	0.26	97
0.5	2.26	89	0.24	95	0.93	88	0.25	95
1.0	2.05	88	0.40	95	1.35	85	0.28	94
2.0	1.78	84	0.57	96	1.39	81	0.35	95
5.0	2.92	78	0.70	99	1.31	75	0.29	97
10.0	3.79	74	0.33	107	1.21	72	0.54	102

* Without Myers - Tracy signal compensation.
† With Myers - Tracy signal compensation.
‡ CV, coefficient of variation.

Table 5. Effect of potassium chloride concentration on the determination of 10 µg ml⁻¹ of manganese

KCl matrix, % m/V	Cross-flow nebuliser				Ebdon nebuliser			
	A*		B†		A*		B†	
	CV‡, %	Signal recovery, %	CV‡, %	Signal recovery, %	CV‡, %	Signal recovery, %	CV‡, %	Signal recovery, %
0.0	0.77	100	0.39	100	0.91	100	0.47	100
0.1	1.84	94	0.50	95	1.52	95	0.22	97
0.2	1.79	90	0.37	95	1.64	90	0.81	95
0.5	2.73	88	0.75	94	1.21	88	0.83	95
1.0	1.61	82	0.42	92	1.16	84	0.42	93
2.0	3.17	78	0.69	89	1.59	83	0.40	92
5.0	2.50	66	1.20	85	1.40	73	0.31	86
10.0	2.35	54	1.33	80	1.27	66	0.70	82

* Without Myers - Tracy signal compensation.
† With Myers - Tracy signal compensation.
‡ CV, coefficient of variation.

procedure reduces the correlated noise in the system. A comparison of related sensitivities obtained with and without signal compensation can also be made by reference to the data in Table 4. In the absence of compensation, increasing signal depression is observed with increasing potassium chloride concentration, irrespective of which nebuliser is employed. However, signal losses are reduced to less than 5% when signal compensation is used. Interestingly, the bias in this instance appears to reach a maximum at a concentration of about 1% potassium chloride, and approaches zero at higher levels. At a 10% potassium chloride content, an over-compensation is made. Clearly, this indicates a difference in the behaviour between scandium and copper with respect to the interferent. In comparison with the depressions of 25–30% obtained without compensation, however, in practical terms it is a secondary effect.

A similar procedure was adopted for the measurement of manganese in the potassium chloride matrix. The results are presented in Table 5. Again, it can be seen that without signal compensation, the high dissolved solids nebuliser yields better precision in the salt matrix than does the cross-flow nebuliser. However, using Myers - Tracy signal compensation, almost all of the coefficients of variation obtained using either nebuliser are substantially less than 1%, except at higher concentrations, where there is some indication that precision begins to deteriorate for the cross-flow system. The benefits in terms of precision though, are not as good as those obtained in the equivalent study for copper, with an average improvement of approximately 3-fold. The results obtained without signal compensation show evidence of substantial interference, with signal losses as high as 46 and 34% for the cross-flow and high dissolved solids nebulisers, respectively. The interference

effect increases with increasing potassium chloride content as might be expected, and appears to be somewhat worse for the cross-flow nebuliser. This could be attributed to the fact that the cross-flow nebuliser is prone to clogging. However, no difference was observed in signal recoveries using the two nebulisers for copper and the results are more likely to reflect a combination of transportation and interference phenomena. When signal compensation was employed, the signal losses were reduced by a factor of two in both instances. It is evident however, that a substantial bias remains and has not been compensated for, by using the Myers - Tracy procedure.

Ionisation and excitation potentials for manganese, copper and scandium are shown in Table 6. The sum of the excitation and ionisation potentials for a given species allows the categorisation as hard or soft lines.^{21,22} Manganese and scandium lines used in the present work are classed as hard, as $V_{\text{sum}} > 12$ eV. However, the summed potential for Sc II is marginally closer to that of Cu I, a soft line, than to Mn II, a typical hard line. Using the standard (or default) plasma

Table 6. Excitation and ionisation potentials

Spectral line/nm	$V_{\text{excitation}}$ / eV	$V_{\text{ionisation potential}}$ / eV	V_{sum} / eV	Class*
Mn II 257.610	4.81	15.63	20.45	Hard
Sc II 424.638	2.91	12.80	15.71	Hard
Cu I 324.754	3.81	7.72	11.53	Soft

* Categorised in the manner described in reference 20.

Table 7. Effect of varying plasma power on signal recovery for manganese*

Power setting/ W	Signal recovery, %	CV† of the 2% m/V KCl matrix, %	CV† of 10 µg ml ⁻¹ of aqueous manganese standard, %
600	92	0.80	0.29
800	93	0.51	0.51
1000	93	0.49	0.35
1200	94	0.63	1.03
1400	96	0.34	0.20
1600	96	1.23	0.72
1800	97	0.57	0.72

* Signal recovery calculated relative to the 10 µg ml⁻¹ aqueous Mn standard solution.

† CV, coefficient of variation.

conditions, it is evident that the internal standard response more closely approaches that of copper than that of manganese. An investigation was carried out to determine whether alteration of the plasma conditions would result in a better correlation between the Mn II and Sc II responses.

Signals from solutions containing 10 µg ml⁻¹ of manganese, with and without 2% potassium chloride were measured using the high dissolved solids nebuliser. It was found that adjusting the nebuliser gas flow-rate in the range 0.6–1.0 ml min⁻¹ did not influence the signal recovery to any great extent. The plasma power setting was varied in the range 600–1800 W covering the full range of the generator output. The results are presented in Table 7. The signal recovery was improved by increasing the plasma power setting. It is possible that further improvements may be obtained by adopting a more wide ranging multi-variate optimisation strategy. The precision values obtained in the potassium chloride matrix are comparable to those obtained for aqueous manganese solutions. The measurements were taken after allowing only a 15-s power equilibration delay. Whilst this might have a deleterious effect on the stability, it does represent the situation where plasma parameters are changed during a sequential multi-element run. Experience with the system indicates that typically coefficients of variation of 0.2–0.4% are obtained for a given fixed power setting.

Conclusions

It has been demonstrated that Myers - Tracy signal compensation can provide considerable improvements in the analytical precision for elements which exhibit different behaviour in the

ICP. The results indicate, however, that correcting for interference effects may require a systematic optimisation procedure on individual elements to achieve the best results. Although the use of a single internal standard is considered inappropriate for simultaneous ICP-AES,^{8,9} there may be some scope for improving the methodology in sequential multi-element analysis by adopting this approach. Work is proceeding to characterise the Myers - Tracy signal compensation system for a wide variety of elements and matrices.

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