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## Sources of variability in cation analysis for a quantitative exfoliation corrosion resistance test

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### Abstract

Exfoliation corrosion of some high-strength aluminum alloys results in delamination of the metal surface resulting in a reduction of mechanical properties. The susceptibility is a strong function of the metallurgical condition of the material. Artificial aging treatments leading to higher strengths generally lead to higher susceptibility to exfoliation. The results of a new, quantitative test for exfoliation resistance based upon solution analysis of dissolution products are presented. Capillary electrophoresis (CE) has been used to quantify the  $Mg^{2+}$  and  $Zn^{2+}$  leached by 10 mM HCl from the thermal oxide of aluminum alloy AA7075 artificially aged to different degrees. An empirical relationship was found between the ratio of  $Mg^{2+}$  to  $Zn^{2+}$  dissolved during the test and the susceptibility of material to exfoliation. The development of the test is discussed with a focus on an analysis of its reproducibility and sources of variance. The primary sources of variability were found to be spatial variations in the composition of the thermal oxide and inhomogeneities in the test solution.

*Keywords:* Corrosion; Aluminium alloys; Metal ions

### 1. Introduction

The susceptibility to exfoliation corrosion of high-strength aluminum alloys limit their performance in aerospace applications [1,2]. Exfoliation corrosion is a type of attack in which the grain boundary regions of the alloy are preferentially dissolved, leading to the precipitation of corrosion products which act to wedge open the boundaries and thereby allow further solution ingress and corrosion to take place. Exfoliation can take place on materials exposed to atmospheric conditions such as those present in seacoast, urban, or industrial environments [1]. Wrought, high-strength aluminum alloys, which contain alloying elements such as Mg and Zn are particularly susceptible to this form of corrosion. During service, this

form of degradation leads to a decrease in the load-carrying capacity of the component. The detection and repair of exfoliation corrosion damage of aluminum alloys used for structural components on aircraft involve substantial costs.

Aluminum alloy AA7075 is an Al–Mg–Zn–Cu alloy used extensively in aerospace structural applications due to its high strength-to-mass ratio [3]. The high strength is achieved by heat treatments which lead to the precipitation of small (sub-micron) particles throughout the material [3,4]. These particles are highly enriched in the alloying elements. Unfortunately, these same precipitates lead to a decrease in the resistance to corrosion [5]. For AA7075, it is generally believed that exfoliation occurs due to the dissolution of the  $MgZn_2$  strengthening precipitates. These precipitates occur preferentially at grain boundaries.

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While the precipitation strengthening process also leads to an increase in the susceptibility of the material to exfoliation corrosion, heat treatment procedures have been developed which mitigate the corrosion, albeit with a trade-off in the mechanical properties. These procedures, known as tempers, have been standardized [6] and are indicated by annotation to the alloy designation. Three commercial tempers are common. AA7075-T651 represents a material which has been thermally treated to give the highest (or peak) strength, but which also has a low resistance to exfoliation. Temper -T7651 was developed to provide improved exfoliation corrosion resistance with a small decrease in strength. Over-aging to temper -T7351 leads to a larger strength decrease (ca. 12–15% lower than -T651), but a substantial increase in the resistance to exfoliation corrosion and stress-corrosion cracking, another form of localized corrosion. The details of the application (e.g., expected stresses and environmental exposure) determine which temper condition is appropriate.

Testing for exfoliation corrosion resistance is regularly performed for quality control, production lot acceptance and as a guide for alloy/temper development. The currently accepted test is ASTM G 34 'Standard Test Method for Exfoliation Corrosion Susceptibility in 2XXX and 7XXX Series Aluminum Alloys (EXCO Test)' [7]. The EXCO test was developed in the early 1970's and consists of a reasonably short-term (typically 48 h) exposure of a material to a solution containing 0.1 M HNO<sub>3</sub>, 4 M NaCl and 0.5 M KNO<sub>3</sub>. At the end of the test, the appearance of the material surface of interest is compared to reference photographs and graded on a letter scale (A through D). The advantages of the EXCO test are its simplicity and its good correlation to long-term exposures [8,9]. The two major disadvantages of the EXCO test are its subjectivity and its non-quantitative nature. The grade given a material can be strongly influenced by the extent of the experience of the grader. The non-quantitative nature of the test impedes the development of new alloys and tempers which may incrementally, but significantly, improve the exfoliation resistance. The lack of a numeric value associated with the resistance can also lead to difficulties in the specification of materials performance for lot acceptance.

An alternative exfoliation resistance test that is

quantitative has been developed [10]. It is based on the analysis of the relative abundance of Mg<sup>2+</sup> and Zn<sup>2+</sup> in solution after a brief (60 min) exposure of the mill-finish thermal oxide of the material, to dilute hydrochloric acid (HCl). The mill-finish thermal oxide (MFTO) is the scale that forms on the external surfaces of the material during the thermo-mechanical processing steps that are used to convert the ingot to plate-form of the desired temper. As part of the test development, the variability in the test results has been quantified and the relative contributions of different sources of variability defined.

## 2. Experimental

### 2.1. Materials

The primary materials used in this research were three commercial 2.5 cm (1 inch) thick AA 7075 plates. Each plate had been tempered to one of the three common commercial tempers (-T651, -T7651, -T7351 [6]). All of the plates had compositions which fell within accepted limits of the following nominal composition (wt.%): 5.6 Zn, 2.5 Mg, 1.6 Cu, <0.5 Fe, 0.4 Si, 0.23 Cr, 0.3 Mn, 0.2 Ti, remainder Al. The material was supplied by Reynolds Metals (RMC, Richmond, VA, USA).

### 2.2. Dissolution test procedure

Specimens 5 cm×5 cm square were cut from the 2.5 cm thick plates. Specimens were subsequently degreased in an ultrasonic bath with either methanol for 5 min or acetone for 5 min followed by methanol for 5 min. The specimens were then rinsed in high-purity water and blown dry with laboratory air. The degreased test specimen was securely fixed in a test rig which exposed a defined area of the MFTO surface, and the 10 mM HCl test solution added. After the 60 min exposure time, the entire test solution was withdrawn with a pipette and stored in clean, high-density polyethylene or polypropylene containers. Aliquots of the test solution (50 μl) were removed and diluted with high-purity water (resistivity=18.2 MΩ/cm) from a Millipore Milli-Q UV Water Purification system (Millipore, Milford, MA, USA). The resulting samples were analyzed for

cation content. For the purposes of this paper, the term aliquot refers to a 50  $\mu\text{l}$  volume of test solution removed for analysis, while sample refers to a diluted aliquot that was actually analyzed for its ionic content.

The vast majority of testing used an exposed area of 11.6  $\text{cm}^2$  and a test solution volume of 7.2 ml. As discussed below, a few tests used an exposed area of 65–68  $\text{cm}^2$ . Due to experimental constraints in test cell modification, a test solution volume of 30.0 ml was used. These two test conditions represent exposed area:test solution volume ratios of 1.6 and 2.2, respectively.

### 2.3. Analytical methods

Analysis of the ionic composition of the samples was performed by CE. For confirmation, analysis of some solutions was repeated using inductively coupled plasma (ICP) at RMC.

All solution analyses performed at the University of Virginia were conducted using a Waters Quanta 4000 Capillary Electrophoresis System (Waters, Milford, MA, USA). Data acquisition was achieved using a personal computer running Baseline 810 or Millennium (Waters) chromatography software. Fused-silica capillaries were 60  $\text{cm} \times 75 \mu\text{m}$  I.D. (Polymicro Technologies, Phoenix, AZ, USA). The electrolyte consisted of 5  $\text{mM}$  UV Cat 1 (Waters) and 6.5  $\text{mM}$   $\alpha$ -hydroxyisobutyric acid (HIBA) (Waters) at its natural pH of 4.4. Detection was accomplished by indirect UV absorption at 185 nm or 214 nm using a mercury lamp and 185 nm filter or a zinc lamp and a 214 nm filter, respectively. Samples were introduced into the capillaries by hydrostatic injection at 10 cm for 30 s. The separation voltage was 20 kV.

The ICP measurements conducted by RMC were performed using an ARL 3580 system equipped with a corrosion-resistant, Babbington nebulizer. The analyses were performed at 100 W and used a 27 MHz generator. Four standards (EM Science) ranging in concentration from 0.1 ppm to 200 ppm were used to calibrate the system. Test solutions were analyzed for Al, Cu, Mg and Zn. The detection limits were: Al  $\sim$ 1.0 ppm, Cu  $\sim$ 30 ppb, Mg  $\sim$ 0.8 ppb, Zn  $\sim$ 7.0 ppb.

## 3. Results and discussion

### 3.1. Precision and detection limits of CE

Variations due to the CE equipment itself and quantitation include possible variations in the hydrostatic loading, instabilities in the UV source/detector system and quantitation variance due to finite baseline noise. Standards were used to quantify the variability associated with these effects. The concentrations used ranged from 0.2 to 5 ppm. At least five injections were made of each sample, the peaks quantitated and the relative standard deviation (R.S.D.) calculated. Table 1 indicates that the reproducibility of the technique increases with increasing concentration. The decrease in R.S.D. resulted from the improved signal-to-noise ratio, and decreased sensitivity of the quantitation to the selection of peak start and end points with increasing peak size. As shown in Table 1, these sources combine to give a small (2–6% R.S.D.) variability for the individual components and for the ratio, except for the 0.2 ppm standard. The 0.2 ppm standard showed somewhat higher variability, as would be expected, as this is just above the minimum detection limit (MDL) for  $\text{Zn}^{2+}$  (150 ppb). The MDL (defined as three times the baseline noise) for  $\text{Mg}^{2+}$  was 70 ppb, while that for  $\text{Cu}^{2+}$  was 200 ppb under the conditions used.

Standards were also used to test for any effects of the method of sample preparation on the reproducibility of the results. Multiple standards were made independently, injected once, and the response analyzed. Again, the R.S.D. values for  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$  and their ratio are in the range of the R.S.D. for the quantitation, 2–6%. Since this variability was on the order of the variability of the CE technique and peak quantification, there does not appear to be significant introduction of non-uniformity resulting from sample

Table 1  
R.S.D. (%) for multiple injections of the same standard

Concentration of standard (No. of injections)	R.S.D. (%)		
	$\text{Mg}^{2+}$	$\text{Zn}^{2+}$	$\text{Mg}^{2+}:\text{Zn}^{2+}$
0.2 ppm (5)	5.1	6.9	9.3
0.7 ppm (6)	3.4	1.4	3.1
1 ppm (12)	2.7	2.5	3.7
5 ppm (5)	1.4	0.7	1.3

preparation method. Similar testing showed that the effects of sample volume in the range from 100 to 600  $\mu\text{l}$  had no statistically significant effect on the results.

### 3.2. Comparison of CE and ICP

Confirmation of the results obtained by CE was achieved by repeat analysis of some of the samples and standards by ICP. Two sets of dissolution test samples and blind standards were analyzed. The first set consisted of 21 dissolution test samples and 8 blind standards; the second set was comprised of 7 dissolution test solutions and 4 blind standards.

For the regression analyses, CE results or the nominal concentrations of the blind standards were taken as the dependent variable and the ICP results as the independent variable. Table 2 shows the regression parameters for the two sets of blind standards analyzed by ICP. Concentrations ranged from 200 ppb to 50 ppm. Some standards contained equal amounts of each element while others were made to resemble dissolution test solutions in their concentrations of species:  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  in tens of ppm,  $\text{Zn}^{2+}$  in hundreds of ppb to low ppm and  $\text{Cu}^{2+}$  at the hundreds of ppb level. Overall, the summary statistics imply reliable analysis by ICP and excellent correlation with CE.

The slope parameter from the regression analysis of the data in the first set of dissolution test samples suggested that the results obtained by CE were consistently less than those observed by ICP; solution analysis by CE reported concentrations 70 to 85% of that of the ICP method. However, as shown in Fig. 1, the deviation appeared to be a strong function of the component concentration or magnitude of the  $\text{Mg}^{2+}:\text{Zn}^{2+}$  ratio, respectively. The majority of the deviation occurred for  $\text{Mg}^{2+}>10$  ppm,  $\text{Zn}^{2+}>1$  ppm and  $\text{Mg}^{2+}:\text{Zn}^{2+}>13$ . Considera-

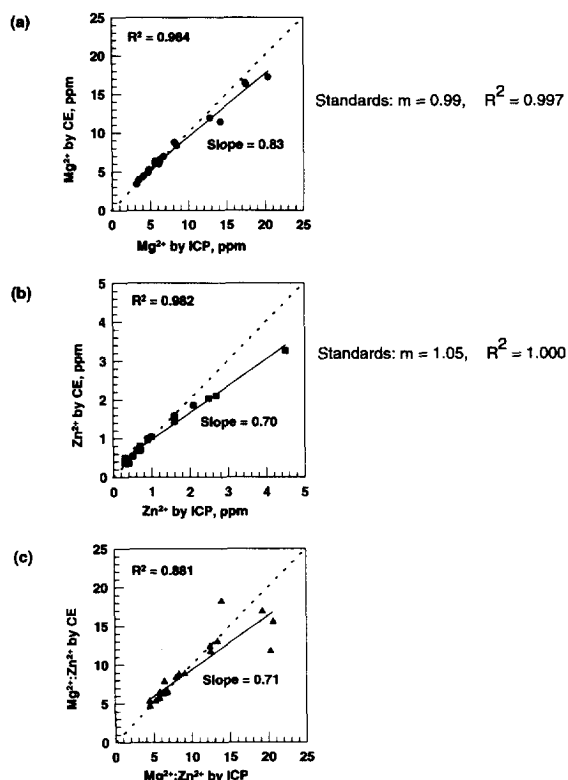


Fig. 1. Comparison of CE and ICP analyses of dissolution test samples of set 1. Note the improved agreement for  $\text{Mg}^{2+}<10$  ppm,  $\text{Zn}^{2+}<1$  ppm,  $\text{Mg}^{2+}:\text{Zn}^{2+}<13$ .

tion of only those data less than these values improved the correlation between the two data sets such that the slopes were  $\geq 0.90$  and  $r^2$  increased from 0.881 to 0.961 for the ratio. The second set of solutions analyzed by both CE and ICP exhibit strong correlations for both  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$ . Note however, that the slope for the ratio is only 0.85. While the differences in the quality of the correlation between the ICP and CE results for the standards and

Table 2  
Summary regression statistics for ICP and CE analyses of standards

Set	No. Samples	$\text{Mg}^{2+}$		$\text{Zn}^{2+}$		$\text{Cu}^{2+}$		$\text{Al}^{3+}$	
		Slope	$r^2$	Slope	$r^2$	Slope	$r^2$	Slope	$r^2$
1	8	1.01	1.000	1.05	1.000	1.04	1.000	0.98	0.998
2	4	0.93	0.908	1.09	0.995	1.01	0.999	0.97	0.981
1 and 2	12	0.99	0.997	1.05	1.000	1.04	1.000	0.97	0.999

the dissolution test samples are not fully understood, some type of matrix effect is clearly involved.

### 3.3. Analysis of solutions from dissolution test

An electropherogram from a sample removed from a dissolution test of a specimen of AA7075-T651 is shown in Fig. 2. The presence of  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  are indicated. Copper was rarely detected, and then at extremely low levels (ca. 100 ppb). The empirical correlation found between the ratio of  $\text{Mg}^{2+}$  to  $\text{Zn}^{2+}$  dissolved from the MFTO and the susceptibility of the material to exfoliation is shown in Fig. 3 for the three commercial tempers. The three plates originated from separate ingots and were processed at different times. Other tests, using a series of materials originating from the same ingot and tempered to different extents, showed the same qualitative trend of decreasing Mg:Zn ratio with increasing resistance to exfoliation [10]. The correlation between known exfoliation resistance for these widely-used tempers and the measurement of the composition of a solution resulting from short-term chemical dissolution

of the MFTO test provides a basis for a simple, quantitative test for exfoliation resistance.

The 95% confidence intervals (calculated using a Student *t*-distribution) indicated in Fig. 3 show the variability found in the measured  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ , and their ratio to be significant. The variability of the measurements is on the order of 15–20% when expressed as the R.S.D. The variability in the EXCO test is generally  $\pm$  one letter grade. While substantially better than the variability associated with the EXCO test, this range of variability in the dissolution results was greater than expected, based upon the known precision and accuracy of CE analysis as discussed in Section 3.1. Fig. 3 shows that the variability in the ratio was not confined to one component ( $\text{Mg}^{2+}$  or  $\text{Zn}^{2+}$ ).

### 3.4. Sources of variability of the dissolution test

As stated above, the variability of the results from samples was higher than the corresponding variability of the CE method obtained from replicate measurements of standards. The following sources of variability have been identified and quantified: inhomogeneities in the aliquots removed from the test solution and spatial variations in the composition of the MFTO.

Although the test solution was mixed prior to sampling, it is conceivable that the test solution was not a homogeneous mixture of the dissolved alloying elements. On a microscopic scale, the MFTO is not uniform; perhaps during the oxide dissolution, particles rich in alloying elements entrained in the oxide were released undissolved into the solution. During aliquot removal and subsequent preparation of samples for analysis, some aliquots may have contained more or less of these particles. Once the particles dissolved in the working sample, different concentrations of dissolved alloying elements would be detected from different samples of the same test solution. To investigate this possibility, the dissolution test was conducted on one -T651 specimen and one -T7351 specimen. Three 50  $\mu\text{l}$  aliquots were taken at each of the following times: 20, 40 and 60 min. A control test was also conducted in which the test specimen was replaced by a plastic block and 7.2 ml of a 5 ppm standards replaced the 10 mM HCl. As can be seen in Table 3, while the -T651 and 5

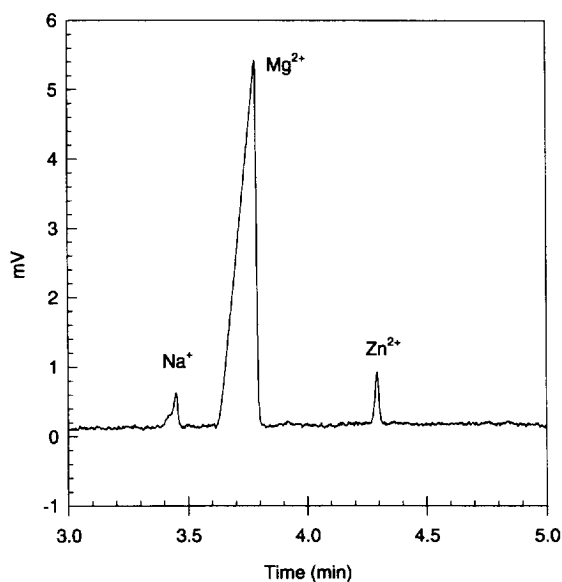


Fig. 2. Electropherogram of dissolution test sample from a specimen of AA7075-T651 showing  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  formed by dissolution of mill-finish thermal oxide in 10 mM HCl after 60 min.

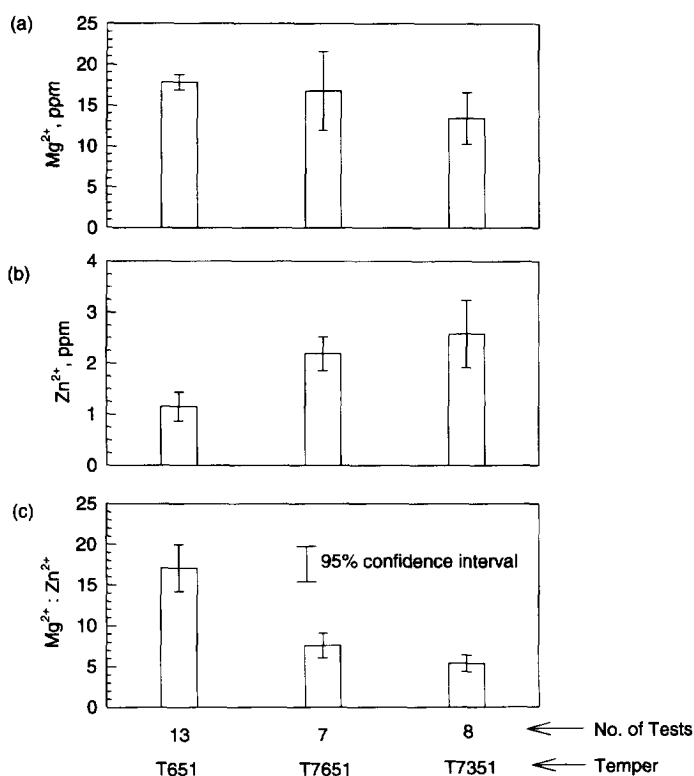


Fig. 3. Concentration of (a)  $Mg^{2+}$ , (b)  $Zn^{2+}$  and (c) the  $Mg^{2+}:Zn^{2+}$  ratio for dissolution samples from the three commercial tempers tested. The number of tests refers to the number of alloy specimens. The EXCO results were: ED for -T651 (poor), EB for -T7651 (fair) and EA for -T7351 (good).

ppm control have R.S.D. values close to that of the individual standards, the samples from the -T7351 specimen have much higher variability. Fig. 4 shows the three electropherograms from the samples pre-

pared from the -T7351 specimen after 40 min. While the variability in the  $Mg^{2+}$  peaks was small, one of the  $Zn^{2+}$  peaks was approximately a factor of two higher than the other two. However, this set of

Table 3  
R.S.D. (%) for dissolution test samples from -T651, -T7351 and control specimens, for aliquots removed after different testing times

Species	Time (min)	Specimen R.S.D. (%)		
		Temper -T651	Temper -T7351	Control
$Mg^{2+}$	20	1.40	15.67	7.05
	40	2.67	2.71	3.44
	60	7.53	6.31	4.36
$Zn^{2+}$	20	3.12	12.79	8.29
	40	6.52	73.40	3.88
	60	7.83	19.55	0.10
$Mg^{2+}:Zn^{2+}$	20	4.54	13.61	1.48
	40	7.34	53.23	1.90
	60	2.19	23.76	4.43

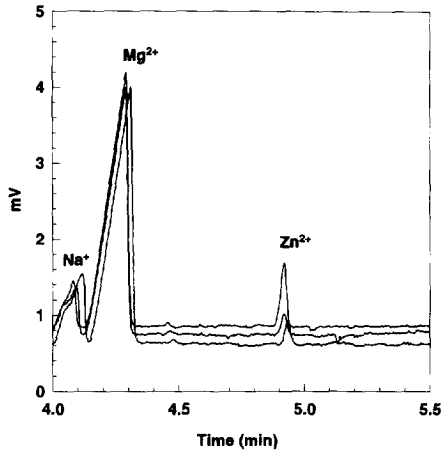


Fig. 4. Electropherograms showing  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  peaks for multiple aliquots taken from the -T7351 specimen at 40 min. Note the significant difference in the  $\text{Zn}^{2+}$  peaks for one of the injections, while all of the  $\text{Mg}^{2+}$  peaks are quite similar in size.

results shows that the variability observed in the dissolution test ratios is not due to sample aliquot handling, as the variability in the standard solution is still within the range of that observed from the study of the quantitation. The  $\text{Na}^+$  peaks were due to contamination from the sample vials used at that time.

Inhomogeneities in the aliquots removed from the test solution, as opposed to variability in the method of sample preparation, is believed to be the source of poor reproducibility exhibited in Table 3 for the samples obtained from the test of the -T7351 specimen. The reasoning for this is best explained by comparing the R.S.D. values for the samples taken at 40 min for the T7351 specimen. The extreme variability in the  $\text{Zn}^{2+}$  content (R.S.D.  $\sim 75\%$ ) was not paralleled by similar variation in the  $\text{Mg}^{2+}$

concentration (R.S.D.  $\sim 2.5\%$ ). If the differences were due to sample preparation (i.e., dilution) then the poor reproducibility would translate to both components since both species were quantified from the same three injections, as shown in Fig. 4. The fact that the results for the three samples taken at 40 min were very different for only one component ( $\text{Zn}^{2+}$ ) imply that the differences in concentration were due to differences in the aliquot compositions. While not understood, the R.S.D. values for samples taken from tests of -T7351 specimen were consistently higher than samples taken from tests of the other tempers.

Another source of variability investigated, was the possibility that macroscopic variations in the spatial composition of the oxide itself existed; that is, the possibility that compositional gradients existed extending over distances on the order of centimeters, within the plane of the plate. To test this proposition, measurements were made in which the exposed area was increased from  $11.6 \text{ cm}^2$  to  $65 \text{ cm}^2$ . The samples were prepared as before and the aliquots were diluted to the same range of concentrations for analysis. The results for the large area test are shown in Table 4. The variability in the results was reduced substantially. When  $11.6 \text{ cm}^2$  was exposed, the R.S.D. for samples from tests of -T651 specimens was 17%. For the large area tests, the variability in the ratio was within the variability of the first four aspects of the test considered. Thus, it appears that large scale spatial variations in the composition of the MFTO exist. Supporting evidence for this was found from a series of X-ray photoelectron spectroscopy studies performed [10]. In that work, nominally identical samples taken from separate areas from the same plate were shown to have substantially different oxide compositions.

Table 4  
Reproducibility of dissolution test, exposed area  $>65 \text{ cm}^2$ , concentrations normalized for differences in volume to area ratio for -T651

Sample	$\text{Mg}^{2+}$ (ppm)	$\text{Zn}^{2+}$ (ppm)	$\text{Mg}^{2+}:\text{Zn}^{2+}$
1	19.85	0.90	22.06
2	18.91	0.90	21.19
3	20.33	0.81	22.77
4	19.85	0.88	22.70
5	19.36	0.94	20.70
Mean	19.66	0.90	21.89
R.S.D. (%)	2.75	2.17	4.19

#### 4. Conclusions

The dissolution test described provides a good indicator of the susceptibility of aluminum alloy 7075 to exfoliation corrosion via the measurement of  $Mg^{2+}:Zn^{2+}$  ratio. Tempers susceptible to exfoliation were found to have  $Mg^{2+}:Zn^{2+} > 10$ . However, sufficiently large areas ( $> 65 \text{ cm}^2$ ) must be tested to ensure that representative results for the material are obtained, due to spatial variations in the composition of the MFTO. CE analysis provides comparable results to ICP analysis over a range of  $Mg^{2+} < 10$  ppm,  $Zn^{2+} < 1$  ppm and a  $Mg^{2+}:Zn^{2+} > 13$ . Outside this range, matrix effects led to differing matrix effects in the two analysis methods. Macro-scale spatial variations in the oxide composition, and inhomogeneities in the sampling of the test solution were the dominant sources of variability of the dissolution test results.

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