

# Determination of Lead Leaching Migration from Crystal Glass by Square Wave Stripping Voltammetry

Lorraine M. Whitney and  
Michael J. Hynes\*  
Department of Chemistry  
National University  
of Ireland  
Galway, Ireland  
Tel: +353 (0)91 524411  
Fax: +353 (0)91 525700  
E-Mail:  
michael.j.hynes@ucg.ie

\* Corresponding author

*Lead migration from lead crystal stemware has been determined by square wave stripping voltammetry. The article under test is filled with 4% (v/v) acetic acid, the solution recommended by ISO 7086/1, and allowed to stand for 24 hours at 22 °C. The deposition is carried out at -0.7 V vs. an Ag/AgCl reference electrode for three minutes. Time of deposition may be varied depending on the quantity of lead leached. Lead is determined using the method of standard additions.*

The problem of lead release from glassware and ceramicware has been a matter of concern to regulatory agencies such as the US Food and Drug Administration (FDA) for some time. An expert panel convened by the World Health Organization (WHO) in 1976 recommended sampling methods, testing methods and limits for release of toxic materials from glass and ceramicware which are in contact with food or beverages. The recommendations have resulted in ISO 7086/1, which outlines the experimental test procedures, and ISO 7086/2, which sets the limits for release of lead (and cadmium).

Lead crystalware contains percentages of lead oxide which range from 4% in light crystal to 32% in heavy lead crystal. While 32% lead crystal was popular in years past, much of the crystal now produced contains approximately 24% PbO. This enables it to comply with EU Directive 69/493/EEC (1), under which glass may not be called crystal unless it contains at least 24% PbO. In addition, certain other re-

quirements with respect to density and refractive index must be met.

In 1991, a paper published by Graziano and Blum (2) caused consternation in the lead crystal industry. In this paper, the authors reported the results of tests they had carried out on lead migration (leaching) from decanters in which wine and spirits were stored. Despite the fact that previous workers had published similar results (3, 4), the Graziano paper received worldwide publicity and articles appeared in newspapers, periodicals and magazines questioning the safety of lead crystal stemware. In response, the International Crystal Federation (ICF), an umbrella group of European and US crystal manufacturers which was set up in April 1991, undertook an urgent investigation of the problem. International Standards ISO 7086/1 and 7086/2 set the limits for release of lead (and cadmium) from glassware and ceramicware in contact with food. The test consists of filling the container with 4% (v/v) acetic acid and leaving it to stand at 22 °C for

24 h. The maximum permissible release of lead from small hollow-ware (<600 mL) is 5 mg l<sup>-1</sup> and from large hollow-ware (>600 mL) is 2.5 mg l<sup>-1</sup>. The ICF has adopted voluntary standards for lead migration which are significantly lower than those demanded by the ISO standard. These are 1.5 mg l<sup>-1</sup> for small hollow-ware and 0.75 mg l<sup>-1</sup> for large hollow-ware. In addition, they recommend that wine or spirits should not be stored in decanters for extended periods unless the decanters have been treated to eliminate lead migration (5). Wines themselves may contain lead in the range 1 - 500 µg l<sup>-1</sup>. The state of California, under Proposition 65, has much stricter limits on lead release. The use of lead crystal cannot result in ingestion of more than 5 µg of lead per day.

ISO 7086/1 recommends the use of an atomic absorption spectrometer having a minimum sensitivity of 0.50 µg l<sup>-1</sup> lead for 1% absorption. However, this is not sufficiently sensitive for determination of lead migration for much of

the lead crystal produced today and is certainly not sufficiently sensitive to determine lead migration from crystal which has been treated to either eliminate or greatly reduce lead migration. Lead migration in such glass when tested using the ISO test can be less than  $10 \mu\text{g l}^{-1}$ . Graphite furnace AA is suitable for determining lead at these concen-

trations. However, the equipment is expensive and requires a high degree of user competence. In order to overcome these difficulties, E.J. Payne Ltd. developed the SA4000 Scanning Analyser (6). This is basically a stripping voltammetry device which uses disposable electrodes which are used for a single determination. The range of the

current instrument is  $40 - 1,500 \mu\text{g l}^{-1}$  and it is clear that the lower limit is insufficient for studying lead migration from treated crystal.

As part of our investigations into the effects of acid polishing on hand-cut lead crystal we need to determine lead migration over a wide range of lead concentrations. Apart from the E.J. Payne device, there is no reference in the literature to the use of stripping voltammetry for the determination of lead migration from crystal glass. This paper describes a method for the determination of lead migration from glassware, in particular lead crystal glass. Stripping voltammetry is a method that has both low detection limits and moderate costs in the determination of several metals.

### Experimental

Voltammograms were obtained using a BAS CV-50W Electrochemical Analyser (Bioanalytical Systems, West Lafayette, IN) fitted with a Controlled Growth Mercury Electrode (CGME) from the same manufacturer. An Ag/AgCl reference electrode and a platinum counter electrode were used. While Osteryoung Square Wave Stripping Voltammetry (OSWSV) is but one of a number of different waveforms available on the CV-50W software, it is widely applicable and was found to provide excellent results in the current work.

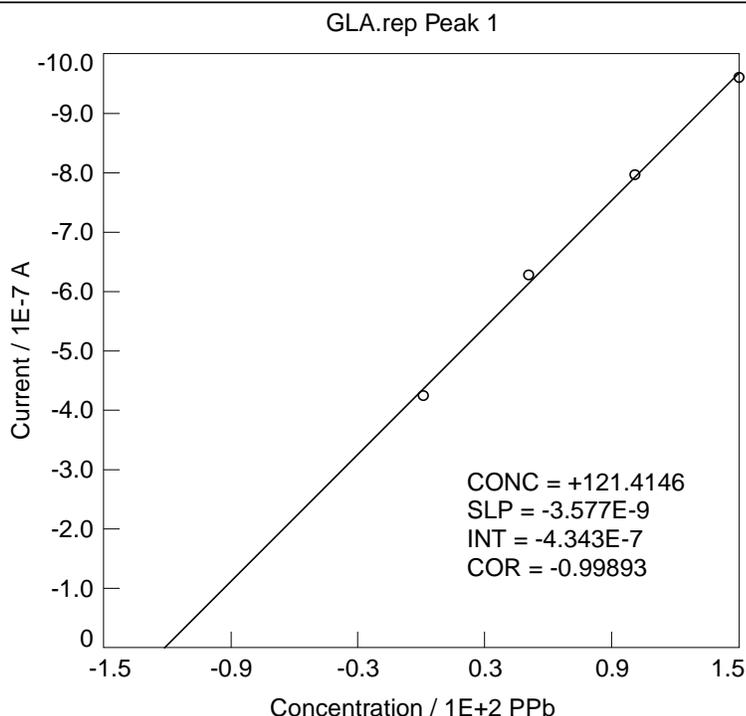
### Procedure and results

The stemware to be tested was filled with 4% (v/v) aqueous acetic acid and allowed to stand at  $22^\circ\text{C}$  for 24 h. A 10 mL aliquot of this solution was placed in the electrochemical cell then purged with Argon to remove dissolved oxygen present. Control experiments demonstrated that no added electrolyte was required. This was probably due to the acidity of the solution.

The CGME was used in the static mercury drop electrode (SMDE) mode. Deposition was performed at  $-0.70 \text{ V}$  vs. the Ag/AgCl electrode for three minutes while

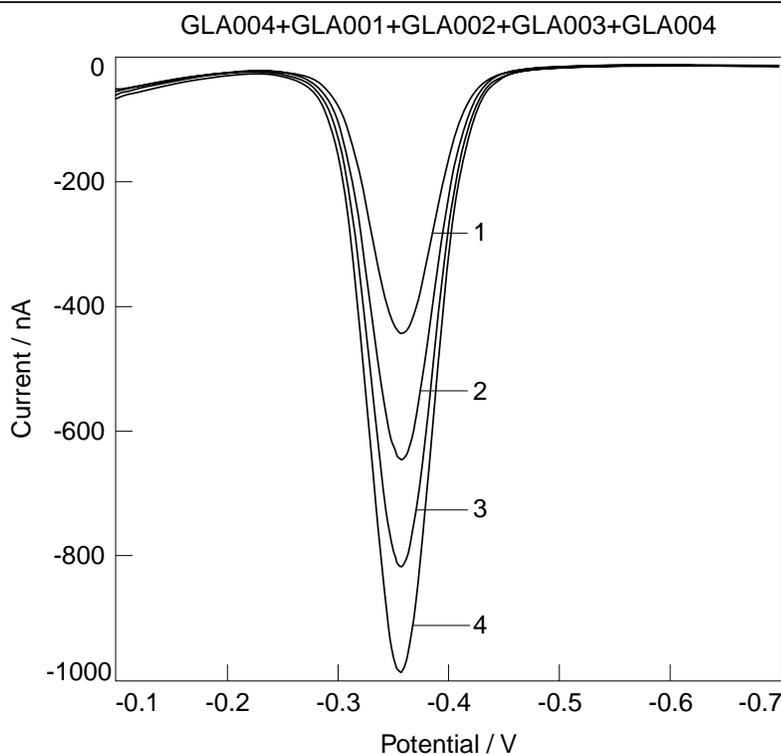
#### F1

Standard additions plot obtained by measuring lead migration from a commercially available beer mug using 4% acetic acid. A 10 mL sample was used and 0.1 mL aliquots of 5 ppm standard lead solution (i.e. 50 ppb spikes) were added.



#### F2

Voltammograms used to produce plot in F1: (1) sample; (2) + 50 ppb  $\text{Pb}^{2+}$ ; (3) + 100 ppb  $\text{Pb}^{2+}$ ; (4) + 150 ppb  $\text{Pb}^{2+}$ .



the stripping voltammogram was recorded from -0.70 V to -0.10 V, using the instrument parameters listed below:

OSWSV	
Initial Potential	-0.700 V
Final Potential	-0.100 V
A.C. Amplitude (mV)	25
Frequency (Hz)	15
Step E (mV)	4
Deposit time (sec)	180
Knock	on
Mode	SMDE
Purge time (min)	5
Drop size	M

After the initial voltammogram was recorded, the sample in the electrochemical cell was spiked with lead using a micropipette. It is generally recommended that the first spike should increase the expected concentration of the analyte by approximately 50% (7). Voltammograms were recorded for three additions of lead. All calculations were carried out using the BAS CV-50W control software. This utilised the peak current for each lead spike, together with the input concentrations, to draw a standard additions plot.

**F1** shows a typical standard additions plot obtained by measuring lead migration from a commercially available beer mug using 4% acetic acid. A 10 mL sample was used and 0.1 mL aliquots of 5 ppm lead solution (i.e., 50 ppb spikes) were added to enable the lead concentration of the sample to be determined. The measured data yielded a

concentration of 121 ppb lead in the test solution. **F2** is an overlay plot of the voltammograms obtained.

### Discussion

It is clear that stripping analysis using the BAS CGME is a satisfactory method for the determination of lead migration from lead crystal. The method has the advantage that, compared to furnace atomic spectroscopy, the capital costs are low and the method is less dependent on the competence of the user. While the SA4000 Scanning Analyser has advantages in a production environment in that it can be used by relatively unskilled personnel, the lower limit of usability is 40 ppb. Many items of hollow stemware, in particular those which have been treated to reduce lead migration, give lead migration values of less than 10 ppb when tested according to ISO 7086. It is clear that the CV-50W can be used to differentiate between various treatment procedures at these levels of lead migration.

The stripping method described above is very flexible in that the deposition time may be varied to suit the expected levels of lead migration. Even concentrations of the order of 1 ppb are readily determined. While the method described above used standard additions, in a routine production process, a calibration curve could be used. This would give greatly reduced times of analysis.

Another very important property associated with the SMDE is the fresh surface provided by each new drop, so that no electrochemical cleaning is necessary. This is comparable to the use of disposable electrodes and contributes greatly to the reliability of the method. The quantity of inert gas and mercury used in an individual analysis with this procedure is very small, resulting in minimal costs compared to furnace AA or the SA4000. Furthermore, the mercury may be readily recovered after use, thus eliminating waste disposal problems.

### Acknowledgement

This work was supported by Forbairt and Galway Irish Crystal under the Industry-University Applied Research Grants Scheme.

### References

1. 69/493/EEC, Council Directive of 15 December 1969 on the approximation of the laws of the Member States relating to crystal glass. OJ, 1969. L326: p. 599-602.
2. J.H. Graziano and C. Blum, *The Lancet*, 337 (1991) 141-142.
3. H. Scholze and R. Sauer, *Zeitschrift für Glaskunde* 47,7 (1974) 49-152.
4. E.A. DeLeacy, *Med. J. Aust.* 147 (1987) 622.
5. M.J. Hynes and B. Jonson, *Chem. Soc. Revs.* (1997) 133-145.
6. E. J. Payne Limited, 1 Belgrave Road, Longton, Stoke-on-Trent ST3 4PR, Staffordshire, England.
7. M.J. Hynes, *Irish Chemical News, Autumn* (1989) 25-27.