

## SHORT PAPER

## Determination of Metals in Poly(vinyl chloride) by Atomic Absorption Spectrometry

## Part 2.\* Determination of Lead and Magnesium in Samples of Poly(vinyl chloride) with a High Content of Alkaline Earths

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This is a continuation of the study of the use of EDTA in ammonia solution to dissolve the precipitate formed when a sample of PVC with a high content of alkaline earths is attacked with sulphuric acid and hydrogen peroxide. The method is used to determine lead and magnesium, and is both rapid and reliable.

**Keywords:** Poly(vinyl chloride) analysis; lead determination; magnesium determination; flame atomic absorption spectrometry

Poly(vinyl chloride) (PVC) is now widely used, in part due to the use of stabilising agents. Many of these agents are metallic and, therefore, can be determined easily by atomic absorption spectrometry. However, not much work has been carried out in this area.

To dissolve the sample, Mendiola *et al.*<sup>1</sup> tested five different methods and found that treatment with sulphuric acid and hydrogen peroxide gave the most satisfactory results. Although in the Mendiola study, 30% *m/m* hydrogen peroxide was used, Taubinger and Wilson,<sup>2</sup> in a study that was later extended by the Analytical Methods Committee,<sup>3,4</sup> pointed out the advantages of using this reagent at 50% *m/m*. Using this procedure, lead,<sup>1</sup> calcium and barium,<sup>5</sup> cadmium and zinc,<sup>6</sup> and tin<sup>8</sup> have been determined in PVC by atomic absorption spectrometry.

Difficulties arise in this type of attack when the PVC sample contains alkaline earths or lead, because, under these conditions, the corresponding insoluble sulphate precipitates out. Mendiola *et al.*<sup>1</sup> solved this problem by centrifuging the precipitate, dissolving it in nitric acid and determining the elements in the two resulting solutions by atomic absorption spectrometry. This procedure considerably lengthens the determination.

In Part 1<sup>9</sup> we proposed the use of EDTA in ammonia solution to dissolve the precipitate formed when a PVC sample containing appreciable amounts of alkaline earths or lead is attacked with sulphuric acid and hydrogen peroxide. It was found that calcium, aluminium and antimony could be determined rapidly by atomic absorption spectrometry using this method, and that the reagents used did not alter the atomic absorption of these metals if the analyte solution is sufficiently diluted and the correct conditions are maintained.

In this work, the study was extended to include the determination of lead and magnesium by atomic absorption spectrometry in samples of PVC with a high alkaline earth content.

Basic lead salts are amongst the most important stabilisers for PVC, while magnesium oxide gives it greater hardness and rigidity. The results obtained in determining these elements are comparable, both in speed and accuracy, to those for calcium, antimony and aluminium.

## Experimental

## Reagents

Concentrated sulphuric acid, *sp. gr.* 1.84.

Hydrogen peroxide, 30% *m/m*.

Concentrated ammonia solution, *sp. gr.* 0.89.

EDTA solution, 4% *m/V*. Dissolve 4.00 g of EDTA (disodium salt) in 100 ml of water with a few drops of ammonia.

Standard lead solution, 1000  $\mu\text{g ml}^{-1}$ . Dissolve 1.60 g of lead nitrate in 50 ml of 1% *V/V*  $\text{HNO}_3$  and dilute to 1 l with 1% *V/V*  $\text{HNO}_3$ .

Standard magnesium solution, 1000  $\mu\text{g ml}^{-1}$ . Dissolve 1.00 g of magnesium in 25 ml of 6 M HCl and then dilute to 1 l with distilled water.

All solutions were prepared with analytical-reagent grade chemicals and re-distilled water, and were kept in polyethylene containers. Solutions of lower concentrations of these reagents were prepared each day by diluting the standard solutions.

## Apparatus

A Perkin-Elmer Model 3030 atomic absorption spectrometer fitted with the appropriate Pye Unicam hollow-cathode lamps was used. The standard system of nebulisation and the corresponding burner for an air-acetylene flame (10-cm slit) were used.

The instrument parameters used in measuring the atomic absorption of lead and magnesium are given in Table 1.

In determining magnesium, two different sets of working conditions were used. For the highest sensitivity (distance of burner below the optical axis 7.5 mm) there is only a small linear range and these conditions were only used for extreme dilutions of the sample. In all other instances, the conditions of lower sensitivity, but with a greater linear range, were preferred.

## Preparation of the Sample

The sample preparation procedure described previously was followed.<sup>9</sup>

## Procedure

Determination of lead and magnesium using a calibration graph

Calibration graphs in the concentration ranges indicated in Table 1 were prepared using standard solutions of these

\* For Part 1 of this series, see reference 9.

**Table 1.** Instrument parameters used in the atomic absorption spectrometry

Element	Wavelength/nm	Lamp current/mA	Flame	Distance of the burner below optical axis/mm	Working range/ $\mu\text{g ml}^{-1}$	Sensitivity/ $\mu\text{g ml}^{-1}$
Lead . . . . .	217.0	5	Air - acetylene (pale blue, oxidising)	7.5	0-10	0.23
Magnesium . . . . .	285.2	6	Air - acetylene (pale blue, oxidising)	25.0	0-2	0.016
	285.2	6	Air - acetylene (pale blue, oxidising)	7.5	0-0.5	0.010

**Table 2.** Results of recovery assays

Element	Metal found in sample/mg	Metal added/mg	Total metal found/mg	Recovery, %
Lead . . . . .	2.29	2.65	4.98	100.8
	2.34	2.65	4.99	100.0
	1.99	2.65	4.64	100.0
	2.34	2.65	4.96	99.4
	1.84	2.49	4.34	100.2
	2.53	2.49	5.03	100.2
	Mean . . . . .			
Magnesium . . . . .	1.04	1.29	2.30	98.7
	1.23	1.29	2.51	99.6
	1.13	1.29	2.39	98.8
	0.97	1.29	2.23	98.7
	0.97	1.29	2.25	99.6
	1.24	1.29	2.49	98.4
	Mean . . . . .			

elements. The sample solutions were diluted between 5- and 10-fold for the lead determinations and between 10- and a 100-fold for the magnesium determinations.

#### Determination of lead and magnesium by standard additions

The sample solutions were diluted five times for the lead determinations and ten times for magnesium. To a series of 25-ml calibrated flasks, add 20 ml of the dilute solutions together with increasing, known amounts of the elements to be determined, diluting finally to 25 ml with distilled water.

#### Measurement conditions

The sample solutions are nebulised and the atomic absorptions of lead and magnesium are measured under the conditions given in Table 1. For magnesium the distance of the burner below the optical axis was 25.0 mm when the standard solution was diluted 10-fold and 7.5 mm when it was diluted 100-fold.

## Results and Discussion

### Attack of the Sample

The general characteristics of the dissolution of the samples were given in Part 1.<sup>9</sup>

Recovery assays of lead and magnesium were carried out. As PVC samples with known concentrations of the metals under investigation were not available, the assay was carried out by adding 1 ml of a solution of these metals to the sample before the dissolution. The dissolution was carried out as described previously, and the lead and magnesium contents were determined using calibration graphs as indicated in the procedure.

The results are given in Table 2. The recoveries of lead were entirely satisfactory, but those of magnesium were slightly low. However, the difference is so small that significant losses

of magnesium during the dissolution of the sample can be ruled out.

### Effect of the Reagents on the Atomic Absorption of the Elements

In order to prepare calibration graphs for the pure solutions of magnesium and lead, the effect of the reagents used in the dissolution of the sample on the atomic absorption of magnesium and lead was studied.

In the determination of lead, a dilution of the treated sample to a volume of 500 ml or more with distilled water is necessary, to ensure that there is no modification of the atomic absorption signal due to the presence of the reagents. A volume of 1000 ml or higher is necessary for the magnesium determination. Even under these conditions, when working under conditions of maximum sensitivity (distance of the burner below the optical axis 7.5 mm) certain very slight modifications of the signal are observed (slope modification of less than  $\pm 1\%$ ).

### Analysis of PVC Samples

The method proposed here has been used to determine lead and magnesium in a sample of commercially available PVC with a high calcium content (*ca.* 10%). The lead and magnesium contents were known to be *ca.* 2 and 1%, respectively. These two metals were determined, following the proposed procedure, using both a calibration graph and the standard additions method. The results are given in Table 3.

The results obtained under the described working conditions for both lead and magnesium were acceptable compared with the known approximate percentages of these elements.

The more dilute solutions had higher standard deviations as anticipated and, in general, the standard additions method proved to be less precise than the calibration graph method.

**Table 3.** Determination of lead and magnesium in PVC

Parameter	Lead			Magnesium		
	Calibration graph		Standard additions	Calibration graph		Standard additions
Dilution of original solution . . . .	1 + 4	1 + 9	1 + 4	1 + 9	1 + 99	1 + 9
Number of determinations . . . . .	8	6	6	8	6	6
Average value/g per 100 g . . . . .	1.96	1.94	1.98	0.99	0.97	1.02
Range/g per 100 g . . . . .	1.92-1.99	1.86-2.05	1.96-2.01	0.97-1.00	0.86-1.03	0.97-1.04
Standard deviation/g per 100 g . . . .	0.029	0.074	0.030	0.014	0.075	0.043
Relative standard deviation, % . . . .	1.5	3.8	1.5	1.4	7.7	4.2

**Table 4.** Analytical conditions of determinations

Element	Minimum dilution of standard solution for which there is no effect from dissolution reagents	Minimum metal that can be determined in PVC*, %	Interference between metals studied
Calcium . . . . .	10-fold†	2	No
Magnesium . . . . .	10-fold†	0.05	No
Antimony . . . . .	2-fold	1	No
Lead . . . . .	5-fold	0.5	No
Aluminium . . . . .	2-fold‡	1	Ca if Ca : Al > 1

\* For a 0.1-g sample and with an RSD of less than 2%.  
† Not working under conditions of maximum sensitivity.<sup>9</sup>  
‡ Addition of KCl to solutions used to prepare the calibration graphs.

### Conclusion

From the results given here, and those previously in Part 1,<sup>9</sup> we conclude that treatment with EDTA and ammonia dissolves the precipitate formed when samples of PVC with high contents of alkaline earths or lead are attacked with sulphuric acid. Under these conditions, determination by atomic absorption spectrometry of calcium, aluminium, antimony, lead and magnesium, at levels of *ca.* 1%, is both fast and precise. These measurements can be made against aqueous solutions of these elements by simply diluting the samples sufficiently.

Table 4 gives a summary of the results obtained. It can be seen that treatment with EDTA and ammonia can be used to determine lead and magnesium in samples of PVC with lower contents than those indicated in the Table; the sample solution is simply diluted less, but in these instances the calibration graphs must be prepared with the dissolution reagents present.

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Note—Reference 9 is to Part 1 of this series.

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