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Spectrographic Determination of Lead in Pectinous Materials

C. RULON JEPPESEN,* E. JOHN EASTMOND, AND HOPE G. LOGAN
*Western Regional Research Laboratory,*** *Albany, California*

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INTRODUCTION

INVESTIGATIONS in this laboratory on new and extended uses of pectin from apple pomace and citrus fruit waste have shown the need for rapid and reasonably accurate determinations of the amounts of lead in various pectinous materials. It was desired to follow the amounts of lead present in various portions of pectinous solution taken during the process of purification of the pomace extract and to determine the amount in the purified solid pectin product. Solution samples contained from 1.5 to 2.5 percent total solids and from 0.005 to 0.125 percent ash. The solid samples had moisture contents of about 10 percent and ash contents between 0.3 and 0.8 percent. The amount of lead in the pomace extract was of the order of 10^{-7} to 10^{-8} gram per gram of solution and in the solid pectin of the order of 10^{-6} gram per gram of pectin. The use of a spectrographic method for detection and measurement of these trace amounts of lead immediately suggested itself.

Several methods for quantitative spectrographic determination of lead in organic materials have been reported in the literature. Most of these methods[1–6] require wet oxidation of the material to be analyzed and the subsequent preparation of a solution containing the spectroscopic buffer and internal standard. The solution is in turn transferred to the electrode in quantities varying with the type of spectral source employed. This procedure has not proved suitable for the determination of lead in pectin. Attempts to digest the organic matter in the pectinous samples and to prepare workable solutions have thus far proved unsuccessful. We have been unable to eliminate contamination during the digestion process, although precautions have been taken with respect to the purity of reagents and the type of vessels used for manipulations. Contaminations have always been of at least the same order of magnitude and, not infrequently, even greater than the concentration of lead in the original sample. Blanks run simultaneously have failed to give consistent correction factors. This was probably due to the fact that the necessary chemical treatment involved the use of strong hot acids which pick up lead from the containing vessels in unpredictable and variable amounts.

Kent[7] has used samples ashed in a muffle furnace for spectrographic estimation of lead, tin, and silver in wheat products. It was necessary in this method to obtain ash free from carbonaceous material and this required the addition, sometimes repeatedly, of concentrated nitric acid.

Our purpose has been to develop a method that is applicable to pectinous materials and requires a minimum treatment of samples. The method developed utilizes dry samples and thus avoids contamination from chemical reagents and the difficulty of getting samples into solution. It can be applied to the determination of lead in other organic materials as well as in pectin.

ANALYTICAL TECHNIQUE

Preparation of Samples

Unashed pectin would not burn successfully in the light source, since foaming caused rapid loss of the major portion of the sample. Furthermore, excessive background resulted when such samples were excited. The samples were therefore dry-

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* Now at Montana State University, Missoula, Montana.

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[1] J. Cholak, J. Am. Chem. Soc. **57**, 104 (1935).

[2] J. Cholak, Ind. Eng. Chem. Anal. Ed. **7**, 287 (1935).

[3] J. Cholak and R. V. Story, Ind. Eng. Chem. Anal. Ed. **10**, 619 (1938).

[4] O. S. Duffendack, K. B. Thomson, W. C. Lee, and O. G. Koppins, J. Biol. Chem. **126**, 1 (1935).

[5] T. M. Hess, J. S. Owens, and L. G. Reinhardt, Ind. Eng. Chem. Anal. Ed. **11**, 646 (1939).

[6] T. M. Hess, J. S. Owens, and L. G. Reinhardt, *Proceedings of the Seventh Summer Conference on Spectroscopy* (John Wiley & Sons, Inc., 1939), p. 29.

[7] N. L. Kent, J. Soc. Chem. Ind. **61**, 183 (1942).

ashed before excitation. The ashing has the additional advantage of concentrating the lead. For the majority of samples, ashing proved to be of no inconvenience, since ash determinations were necessary for other investigations and the same samples could be used for lead tests.

Pectin samples of about 5 or 10 grams were placed in porcelain crucibles, charred on a hot plate, and ashed in a muffle furnace at 500°C. Pomace extract samples of from 25 to 100 grams were placed in platinum evaporating dishes, evaporated almost to dryness, and ashed in the muffle furnace also at 500°C. The pectin samples required from 10 to 15 hours to ash and were usually left in the furnace overnight. The extract samples required less time, from 2 to 3 hours in most cases. It is not necessary to treat the sample with any acid or subject it to long ashing time in order to obtain a white ash, since the presence of carbonaceous material does not affect the analysis in the present method.

The difficulty of maintaining strictly reproducible excitation conditions for dry powder samples made advisable the use of an internal control method. It was necessary to introduce a constant proportion of the internal standard into each sample since the samples showed variable composition with respect to any of the elements normally present. Because of this variable composition a spectroscopic buffer was also used.

TABLE I. Preparation of samples for spectrographic determination of Pb in pectinous materials.

Mixture No.	% Bi	% Pb	Method of preparation
Primary mixtures			
A (synthetic ash)	0	0	5% Basic magnesium carbonate 25% Calcium carbonate 25% Sodium carbonate 30% Silicic acid 5% Ferrous sulfate 10% Aluminum oxide
B	0	0.0075	0.0075% Pb (as Pb_3O_4) in *A*
C	0	.015	.015% Pb (as Pb_3O_4) in *A*
D	0	.030	.03% Pb (as Pb_3O_4) in *A*
E	0	.060	.06% Pb (as Pb_3O_4) in *A*
F	0	.120	.12% Pb (as Pb_3O_4) in *A*
G	0	.240	.24% Pb (as Pb_3O_4) in *A*
H	0.233	0	.233% Bi (as Bi_2O_3) in lithium carbonate
I (standard-buffer base)	.175	0	1 part *A*, 3 parts *H*
Working curve mixtures			
1	.14	.0015	1 part *B*, 4 parts *I*
2	.14	.003	1 part *C*, 4 parts *I*
3	.14	.006	1 part *D*, 4 parts *I*
4	.14	.012	1 part *E*, 4 parts *I*
5	.14	.024	1 part *F*, 4 parts *I*
6	.14	.048	1 part *G*, 4 parts *I*
Unknown mixtures	.14	?	1 part unknown ash, 4 parts *I*

The sample ash was mixed in a mortar with four times its weight of a base which contained the internal standard and spectroscopic buffer. This base was prepared as indicated in Table I. Bismuth was chosen for the internal standard. The lines Pb 2833A and Bi 2898A react quite similarly to varying excitation conditions, as shown by moving plate studies, and were selected as the analysis lines. Considerable experimentation has shown that lithium carbonate acts very satisfactorily as a buffer. It fuses well with the ash and controls the excitation conditions in the light source at least for the period of time that lead remains in the sample. A "synthetic ash," approximating the composition of a pectin ash, was also added to make samples differing in qualitative composition more nearly alike. This is desirable since large differences in the amounts of certain inorganic salts in the ash of various samples might affect the relative intensities of spectral lines.

The standard samples used to determine the analysis or "working" curve were prepared by adding known amounts of lead to portions of the "synthetic ash." Each of these samples was similarly mixed with four times its weight of the same standard-buffer base, as indicated in Table I.

Excitation Apparatus and Procedure

The low voltage d.c. arc is conveniently adapted to the burning of dry powder samples and was used to excite the spectra. The electric current was supplied from a 250-volt d.c. generator and the current was limited by water-cooled ballast resistors in series with the arc. The electrodes were cut from regular spectroscopic graphite rods. Attempts have been made to increase the stability of the arc by the proper choice of electrode shapes. The electrodes used are shown in Fig. 1. About 15 mg of the ash-base mixture was placed in the circular trough in the lower (+) electrode and subjected to the arc at 15 amperes. In operation, the arc strikes chiefly between the two $\frac{1}{8}$-in. center posts and "wandering" is not as apparent as with the usual central cup electrodes.

Spectrograms were taken with a large quartz Littrow spectrograph. An image of the arc was projected on the collimating lens by the use of a long focus lens at the slit of the spectrograph. A diaphragm of 5-mm height and full-lens width was used immediately in front of the collimating lens to mask the image of the incandescent poles. Under these conditions an exposure of 30 seconds is sufficient to give lines of measurable density. Moving-plate experiments have shown that both lead and bismuth are completely burned from the sample in this time and further exposure only increases background density. The spectrograms are free from appreciable background in the vicinity of the lines used in the analysis (see Fig. 2). A rotating step-sector method was used for calibration of the photographic plates. Eastman Spectrum Analysis No. 1 plates were used and developed for 2.5 minutes in Eastman D-72 developer. Sawyer and Vincent[8] have shown that sector disk calibration curves give consistent results when used on these plates.

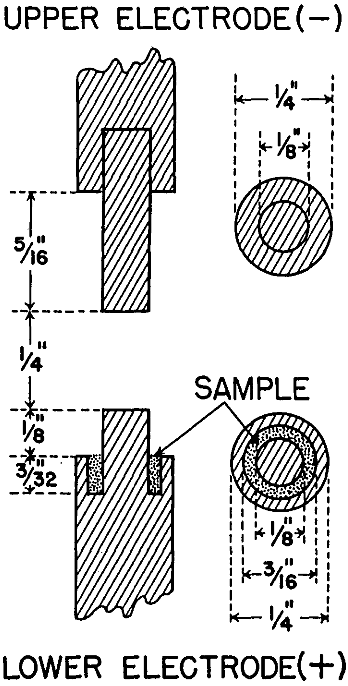

FIG. 1. Longitudinal and cross sections of electrodes used in direct current arc excitation of organic materials.

Measurement and Interpretations of Spectrograms

The densities of the spectral lines were measured with a Sinclair Smith microphotometer-densitometer.[9] The intensity of the line Pb 2833A relative to that of the line Bi 2898A was determined. This relative intensity is a measure of the lead concentration. The working curve, determined experimentally from the synthetic samples with known lead concentrations, is shown in Fig. 3. For a particular analysis the ratio of the intensities of these two lines in the unknown sample was determined and the concentration of lead in the ash-base mixture was read from this curve. The concentration in the original unashed sample was then obtained by simple numerical calculation. In routine analyses in this laboratory the calculation has been simplified by the use of a calculating board equipped with sliding logarithmic scales.[10]

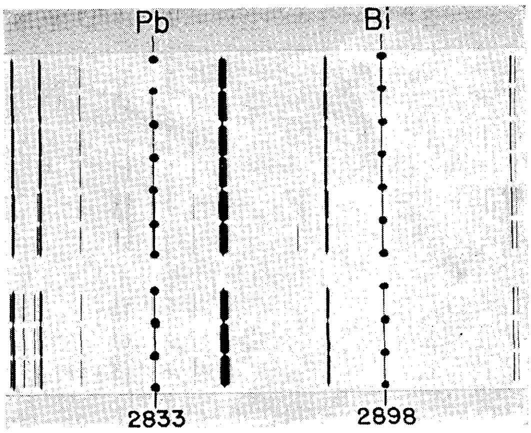

FIG. 2. Sample spectrogram for determination of lead in pectinous materials. The first six spectra are from exposures of the synthetic working curve mixtures. The last three spectra are from triplicate exposures on an unknown mixture.

RESULTS AND DISCUSSION

Precision of Results

The reproducibility of the method is illustrated by the following experiments:

(1) Samples of citrus pectin and apple pomace extract were ashed and mixed as described above. A series of 24 exposures was made on each of these samples. The results are given in Table II.

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[8] R. A. Sawyer and H. B. Vincent, J. Opt. Soc. Am. **33**, 247 (1943).

[9] P. A. Leighton, S. Smith, and F. C. Henson, Rev. Sci. Inst. **5**, 431 (1934).

[10] C. King, J. Opt. Soc. Am. **32**, 112 (1942).

This experiment indicates the reproducibility of the spectroscopic and photometric procedures, if one assumes that the samples have been thoroughly mixed. The maximum deviation of any single result from the mean is 13.6 percent.

TABLE II. Results of repeated exposures on a single sample of solid pectin and a single sample of apple pomace extract.

	Pb (p.p.m.*) in solid pectin		Pb (p.p.m.) in pomace extract	
Exposure No.	Single exposures	Average of triplicate exposures	Single exposures	Average of triplicate exposures
1	2.10		0.46	
2	2.25	2.11	.44	0.46
3	1.98		.49	
4	2.44		.44	
5	2.06	2.27	.41	.43
6	2.32		.45	
7	2.14		.44	
8	1.94	2.11	.46	.45
9	2.25		.45	
10	2.40		.43	
11	2.29	2.31	.45	.45
12	2.25		.48	
13	2.32		.46	
14	2.10	2.16	.48	.47
15	2.06		.46	
16	2.40		.40	
17	2.17	2.20	.44	.43
18	2.02		.44	
19	2.10		.45	
20	2.36	2.32	.40	.43
21	2.51		.45	
22	2.21		.45	
23	2.36	2.17	.44	.46
24	1.94		.48	
Av.	2.21	2.21	0.45	0.45
Maximum deviation from mean	13.6%	5.0%	11.1%	4.5%
Standard deviation from mean	7.4%	3.7%	5.1%	3.6%

* Parts per million. Results are given in parts lead per million parts of original sample.

The increased precision obtained when averages of several exposures of a sample are used is also apparent from Table II. Averages are listed for successive groups of three exposures. Such averages show a maximum deviation of only 5.0 percent. All routine analyses have been made with three or more exposures wherever size of the sample permitted. Even though there is a greater chance for inhomogeneity with the dry powder samples, these results are comparable with those reported for solution samples evaporated on electrodes and excited in the d.c. arc. Cholak[2] gives results of repeated exposures on single samples that show maximum variations as high as 15 percent. He also reports that averages of five exposures show maximum variations around 10 percent of amounts known to be present.

(2) Six samples of the same citrus pectin and six of pomace extract were individually ashed and mixed with standard-buffer base. A group of three exposures was made for each sample, just as would be done if the samples were being run in a routine test. The averages of the triplicate exposures are given in Table III. This experiment tests the reproducibility of the entire analytical procedure. It is apparent from comparison with Table II that variations, in addition to those due to the spectroscopic and photometric procedure, are introduced by the sampling,

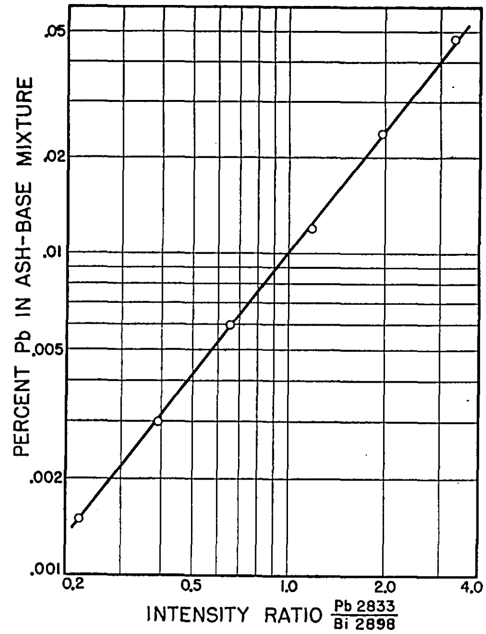

FIG. 3. Working curve for determination of lead in pectinous materials. The six points shown were determined from exposures of synthetic mixtures of known lead concentration.

ashing, and mixing processes. Even so, these results show a maximum deviation of less than 13 percent and a standard deviation of only seven percent. It should be noted that Cholak's[2, 3] reported accuracy tests indicate only the reproducibility of the spectroscopic and photometric procedures, since the samples used for these tests were not subjected to the wet oxidation procedure. Hess, Owens, and Reinhardt,[5, 6] who used wet oxidation and a high voltage a.c. arc, have reported tests on separately ashed samples. Their results show a maximum deviation as high as 20 percent and a standard deviation of approximately 10 percent of the amount of lead known to be present.

TABLE III. Results of triplicate exposures on separately ashed samples.

Sample No.	Pb (p.p.m.) in solid pectin	Pb (p.p.m.) in pomace extract
1	2.29	0.46
2	2.40	.54
3	2.15	.48
4	2.25	.55
5	2.61	.50
6	2.19	.52
Av.	2.32	.51
Maximum deviation from mean	12.5%	9.8%
Standard deviation from mean	7.0%	6.2%

(3) Additional samples were prepared to which known amounts of lead were added before ashing. The lead was added to the solid pectin samples as a 0.1 percent mixture of Pb (as Pb_3O_4) in synthetic ash and to the pomace extract as a 0.001 percent solution of Pb [as $Pb(NO_3)_2$] in distilled water. The calculated amount of lead was added to the original material and ashing then carried out as described above. Again a group of three exposures was made for each sample. The observed results are given in Table IV. The values for the original samples given in the table for purposes of comparison are averages of a large number of trials. The results observed from the samples containing known amounts of added lead are within the limits of error indicated by the above tests.

It can be concluded from this series of tests that, for a single sample analyzed by the method described, the result of triplicate exposures may show a maximum error of approximately 13 percent of the amount present. In general, however, routine results show errors that average less than 10 percent.

It should perhaps be pointed out that both the line Pb 2833A and the line Bi 2898A may show wide self-reversal.[11] At very high concentrations it is possible that self-reversal of the Pb line might affect the precision of measurement. The results of this study indicate that self-reversal is not apparent for the range of concentrations of lead found in organic materials.

Sensitivity of the Method

Concentrations of lead as small as 0.000001 percent in the original sample and 0.005 percent in the ash have been detected and measured. About four mg of ash are required for a single exposure, the ultimate sensitivity (amount of Pb on electrode) thus being about 2×10^{-4} mg. This sensitivity is comparable to that reported for other d.c. arc methods. Cholak[2] reports a sensitivity from 2×10^{-5} to 4×10^{-4} mg but the precision of results was greatly reduced with the smaller amounts on the electrode. A sensitivity of 6×10^{-5} mg, only slightly higher than that of the present method, has been reported[5, 6] for lead determinations with the high voltage a.c. arc.

TABLE IV. Results of test with known amounts of Pb added to samples.

		Pb (p.p.m.)				
			With 1 p.p.m. added		With 3 p.p.m. added	
Material	Trial	Original	Expected	Observed	Expected	Observed
Citrus pectin	*A*	2.21	3.21	3.09	5.21	5.17
	B	2.21	3.21	3.27	5.21	5.52
Pomace extract	*A*	0.48	1.48	1.50	3.50	3.51
	B	0.48	1.48	1.55	3.50	3.69

Unfortunately Kent,[7] who used dry powder samples and a d.c. arc, has made no estimate of either reproducibility or absolute sensitivity.

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[11] *M. I. T. Wavelength Tables* (John Wiley & Sons, Inc., New York, 1939).

It is probable that the present method is more sensitive than his because of the higher current used by us. We have found that sensitivity is noticeably reduced and plate background increased when lower currents are used. Kent's plates showed considerable background which would tend to mask weak lines.

The method described in this paper has the usual advantages of spectroscopic over chemical methods. It is entirely objective and effects considerable saving of time when large numbers of samples are to be analyzed. Ashing the samples, also necessary for chemical methods, requires from 2 to 15 hours. Once the ash has been obtained, however, the analysis can be completed spectroscopically on as many as 8 samples on a single plate in about 4 hours, representing about one-half hour per sample.

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