

# Determination of Arsenic, Lead, Iron, Mercury and Antimony National Spectrographic Laboratory Procedures

## Summary

Four methods are included in this standard test procedure. These methods are performed by National Spectrographic Laboratories, Inc. (NSL), Cleveland, Ohio. Method IA is NSL Procedure 2780 and Method 1B is NSL Procedure 2953 and both describe the determination of arsenic, lead and antimony. Different Methods are used depending on the type of polymer being analyzed. Method II is NSL Procedure 1024 and describes the determination of mercury. Method III is NSL Procedure 2983 and is for the measurement of antimony.

## METHOD IA

### Routine Elemental Determinations in Organic Matrices by Photo-Emission Spectroscopy

#### I. Scope

The method is used to evaluate Carbopol<sup>®\*</sup> and Pemulen<sup>™\*</sup> products manufactured in benzene or ethyl acetate/cyclohexane after suitable ashing and combining with Ga<sub>2</sub>O<sub>3</sub>.

#### II. Apparatus

1. B&L Dual Grating Emission Spectrograph.
2. NSL Model 110-90 Multisource.
3. Baird Atomic Microdensitometer.
4. Torsion Balance (100 mg max.) by Bethlehem.
5. Electronic Balance (160 g/4 place) by Mettler.
6. Ceramic Crucibles, 20 ml capacity – equivalent equipment may be substituted.

#### III. Materials

1. High purity Gallium Oxide (Ga<sub>2</sub>O<sub>3</sub>), Electronic Grade, 5 9s Pure, Eagle Picher.
2. Redistilled Nitric Acid (HN03), Baker.

3. Reagent Grade Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>), Baker.
4. High Purity Graphite, SP2 Grade, National Carbon.

#### IV. Sample Preparation

After physical homogenation and representation are assured, a 1.0 g sample (weighed to the nearest 0.1 mg) is weighed into a clean ceramic crucible. The sample is placed in a clean lab fume hood, combined with 1.5 ml H<sub>2</sub>SO<sub>4</sub> and 0.5 ml HN03 and placed on a hotplate (medium heat) under a heat lamp and charred.

The charred sample is then placed in a laboratory muffle and ashed to completion after a slow temperature ramping at 500°C. The sample is considered ashed when constant weight is observed. The crucible is cooled and weighed to determine the ash content. The inorganic ash is combined with an equal weight of Ga<sub>2</sub>O<sub>3</sub> (30 mg min.).

The inorganic ash+Ga<sub>2</sub>O<sub>3</sub> is returned to the fume hood and a slurry is made in the ceramic crucible by adding 0.5 ml of HN03. The composite is baked to dryness on the hotplate and returned to the laboratory muffle for one hour at 500°C. The crucible is again cooled, weighed and taken to the emission lab for analysis.

The Ga<sub>2</sub>O<sub>3</sub> + residue mixture is transferred from the crucible, ground in an agate mortar, and combined with SP2 graphite (2 graphite: 1 sample) using a torsion balance. The final mixture is shaken in an amalgamator and loaded into graphite electrodes in replicate.

Lubrizol Advanced Materials, Inc. / 9911 Brecksville Road, Cleveland, Ohio 44141-3247 / TEL: 800.379.5389 or 216.447.5000

The information contained herein is believed to be reliable, but no representations, guarantees or warranties of any kind are made as to its accuracy, suitability for particular applications or the results to be obtained. The information often is based on laboratory work with small-scale equipment and does not necessarily indicate end product performance or reproducibility. Because of the variations in methods, conditions and equipment

used commercially in processing these materials, no warranties or guarantees are made as to the suitability of the products for the applications disclosed. Full-scale testing and end product performance are the responsibility of the user. Lubrizol Advanced Materials, Inc. shall not be liable for and the customer assumes all risk and liability for any use or handling of any material beyond Lubrizol Advanced Materials, Inc.'s direct control. The

SELLER MAKES NO WARRANTIES, EXPRESS OR IMPLIED, INCLUDING, BUT NOT LIMITED TO, THE IMPLIED WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE. Nothing contained herein is to be considered as permission, recommendation, nor as an inducement to practice any patented invention without permission of the patent owner.

For further information, please visit [www.personalcare.noveon.com](http://www.personalcare.noveon.com)

## V. Standardization

Secondary standards are fabricated through the controlled addition of pure compounds (representing the elements of interest) to the Ga<sub>2</sub>O<sub>3</sub> base material. The standards are buffered with graphite, mixed, and loaded into graphite electrodes in replicate.

## VI. Instrumental Settings

Upper Electrode: 3954  
 Lower Electrode: 4006  
 Sample Charge: 15 mg  
 Ultraviolet -- 2nd Order  
 Wavelength (A): A 5000-6000  
 B 6000-7000  
 DC Current (Amp.): 18  
 Exposure (Sec.): 120

## VII. Quantitation

The photographic plate generated is interpreted at the wavelengths unique to the element of interest. Calibration/Standard curves are plotted by concentration (wt. %) versus the logarithm of the optical density of the measured line.

The element concentration in the original sample is determined by dividing the quantitative result obtained from the photographic plate by the concentration factor (CF).

$$CF = \frac{\text{Orig. sample wt.}}{\text{g ash} + \text{Ga}_2\text{O}_3}$$

## METHOD IB

### Spectrochemical Test - Quantitative Photo-Emission Determination of Heavy Metals by Sulfide Precipitation

#### I. Scope

This section provides the methodology for evaluating the concentrations of trace amounts of heavy metals (i.e., Pb, Bi, Sn, Sb, Cd, As, Ag, Cu and Mo), or more specifically the sulfide group metals in Carbopol<sup>®</sup> polymerized in ethyl acetate. Coprecipitation of an added or constituent metal is routinely employed.

#### II. Apparatus For Quantitation

- B&L Dual Grating Emission Spectrometer (or equiv.)
- NSL Model 110-90 Multisource (or equiv.)
- Baird Atomic Micro Densitometer (or equiv.)

## III. Sample Preparation (Chemical)

- Place 0.5 to 1.0 g original sample into a 400 ml beaker and "wet ash" with @15 ml concentrated sulfuric acid and additions of 2 ml portions of redistilled nitric acid.

**CAUTION** for maximum efficiency in ashing, the nitric acid should be added carefully to the fuming sample. A watch glass cover and safety equipment are required.

When wet-ashing is complete, the sample is again taken to strong sulfuric fumes after the addition of 40 mg of SpecPure copper metal. After dissolution of the matrix metal is complete, the solution is cooled and diluted to about 200 ml with deionized water in a 400 ml beaker.

- Precipitation. The dissolved/prepped solution is placed into the sulfide hood and hydrogen sulfide gas is bubbled through the solution at a rate vigorous enough to mix and agitate the solution, but also controlled to prevent solution loss through splattering. Hydrogen sulfide is applied for about 20 minutes.

The sulfide solutions are now placed on a hot plate (adjusted to control solution temperatures just below boiling) to promote coagulation of the precipitants. After 30 minutes, the solutions are filtered through #40 Whatman paper, washed with deionized water at least 10 times and folded into a ceramic crucible. The paper and solids are dried on a laboratory hot plate and ignited to a final temperature of 500°C in a laboratory muffle to a constant weight. The crucible is cooled and the ashed material presented to the photo-emission laboratory for evaluation.

An acid/referenced blank is processed frequently to assess any system contamination.

## IV. Sample Preparation (Spectrographic)

The oxidized sample precipitants are removed from the ceramic crucibles and transferred to plastic vials or capsules and mechanically homogenized in an agalgamator unit. Portions of the samples are then mixed with graphite on a 1:1 weight basis using a torsion balance and 15 mg portions are loaded into high-purity graphite electrodes. Samples and standards (see below) are then subjected to identical excitation conditions.

## V. Standardization

High purity copper or molybdenum oxide (previously evaluated in our labs) is spiked with controlled amounts of the elements of interest by using Spex Mix. A master standard is made at a concentration of 0.5% (5000 ppm) and portions of this standard are then diluted with the oxide base to create a range of standards.

## VI. Instrumental Settings

Wavelengths:

- (a) 5000 - 5500Å -- A grating; second order spectra
- (b) 5500 - 6000Å -- B grating;  
Current: 12 amp. -- DC discharge  
Exposure: 45 seconds -- partial consumption

## VII. Quantitation

The photographic plate is interpreted at wavelengths unique to the elements of interest (see below). Calibration/standard curves are plotted by concentration versus the logarithm of the optical density of the line measured. Results obtained by the plate analysis are divided by the appropriate "concentration" factor.

Concentration Factor --  $\frac{\text{Weight (g) of original sample}}{\text{Weight (g) of prepared sample}}$

Element	Wavelengths (Å) Evaluated
As	2780.2, 2860.5
Bi	3067.7, 2898.0, 2938.4
Cd	3466.2, 3404.6, 2980.6
Pb	2833.1, 2663.2, 2802.0
Sb	2528.5, 2877.9, 2598.1
Sn	3175.1, 3262.3, 2840.0, 2863.3
Ag	3280.7, 3382.9

Reference: Applied Inorganic Analysis, Hillebrand, Lindell, Bright and Hoffman, John Wiley & Sons, Inc., New York, 1955 ("Precipitation By the Sulfide Ion", pg. 58).

## METHOD II

### I. Scope

This method covers the analysis of mercury in organic materials by flameless atomic absorption. The range of analysis is .002 ppm to 5000 ppm.

### II. Summary

The sample, dissolved in appropriate acids (nitric or nitric and sulfuric, no hydrochloric should be used) is refluxed in an isolated condenser system to prevent loss of mercury. Mercury is reduced to the metal vapor and is aerated into the flameless atomic absorption unit where the mercury content can be determined.

### III. Apparatus

1. Flask and reflux condenser system with hot plate. (250 ml. flask and 300 mm Graham condenser or equivalent.)
2. Coleman Model 50B Mercury Analyzer.
3. BOD bottles, 300 ml. size.

### IV. Reagents and Solutions

1. HNO<sub>3</sub>
2. H<sub>2</sub>SO<sub>4</sub>
3. 5% Potassium Permanganate Solution
4. 1.5% Hydroxylamine Hydrochloride Solution
5. 10% Stannous Chloride Reagent
6. Mercury Standard Solution (1000 mg Hg/liter)

### V. Procedure

1. A blank must be carried along with the sample.
2. Weigh approximately 0.2 gram sample into a reflux flask and place on condenser.
3. Add 10 ml. of HNO<sub>3</sub> and 10 ml. of H<sub>2</sub>SO<sub>4</sub> through the condenser.
4. Turn on hot plate to set temperature and dissolve or digest sample for minimum of 2 hours.
5. After cooling to room temperature, wash reflux condenser into flask and quantitatively transfer solutions into BOD bottles.
6. If necessary, dilute solution in BOD bottles to 100 ml. but do not exceed 100 ml. volume.
7. Standardize the Coleman unit with a 1.0 ppm standard prepared from the 1000 ppm standard. Follow steps 8 through 10 below.

## VI. Analyzing Samples

8. Add enough 5% Potassium Permanganate to oxidize all the mercury, an excess will show the solution to be purple in color.
9. Add enough 1.5% Hydroxylamine Hydrochloride to reduce any excess Potassium Permanganate. The solution will lose its purple color.
10. Add 10 ml. of 10% Stannous Chloride and immediately place aerator from flameless AA on and read  $\mu\text{g}$  of mercury.

## VII. Calculations

$$\text{ppm Hg} = \frac{\mu\text{g of Hg from sample} - \mu\text{g of Hg from blank}}{\text{Sample weight in grams}}$$

## METHOD III

### I. Scope

This method provides for the evaluation of routine traces of antimony in organic matrices after suitable ashing and combining with  $\text{Ga}_2\text{O}_3$ .

### II. Apparatus

1. B&L Dual Grating Emission Spectrograph
2. NSL Model 110-90 Multisource
3. Baird Atomic Microdensitometer
4. Torsion Balance (100 mg. max.) by Bethlehem
5. Electronic Balance (160 g./4 place) by Mettler
6. Ceramic Crucibles, 20 ml. capacity  
(equivalent equipment may be substituted)

### III. Materials

1. High purity Gallium Oxide ( $\text{Ga}_2\text{O}_3$ ), Electronic Grade, 5 9S Eagle Picher.
2. Redistilled Nitric Acid ( $\text{HNO}_3$ ), Baker
3. Reagent Grade Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ), Baker
4. High Purity Graphite, SP2 Grade, National Carbon

### IV. Sample Preparation

After physical homogenization and representation are assured, 1.0 g. sample (weighed to the nearest 0.1 mg.) is weighed into a clean ceramic crucible. The sample is placed in a clean lab fume hood, combined with 1.5 ml.  $\text{H}_2\text{SO}_4$  and 0.5 ml  $\text{HNO}_3$  and placed on a hotplate (medium heat) under a heat lamp and charred.

The charred sample is then placed in a laboratory muffle furnace and ashed to completion after a slow temperature ramping at 500 degrees C. The

sample is considered ashed when constant weight is observed. The crucible is cooled and weighed to determine the ash content. The inorganic ash is combined with an equal weight of  $\text{Ga}_2\text{O}_3$  (30 mg. minimum).

The inorganic ash with  $\text{Ga}_2\text{O}_3$  is returned to the fume hood and a slurry is made in the ceramic crucible by adding 0.5 ml. of  $\text{HNO}_3$ . The composite is baked to dryness on the hotplate and returned to the laboratory muffle furnace for one hour at 500 degrees C. The crucible is again cooled, weighed and taken to the emission lab for analysis.

The  $\text{Ga}_2\text{O}_3$  and residue mixture is transferred from the crucible, ground in an agate mortar and combined with SP2 graphite (2 parts graphite with 1 part sample) using a torsion balance. The final mixture is shaken in a amalgamator and loaded into graphite electrodes in replicate.

### V. Standardization

Secondary standards are fabricated through the controlled addition of pure compounds (representing the elements of interest) to the  $\text{Ga}_2\text{O}_3$  base material. The standards are buffered with graphite, mixed and loaded into graphite electrodes in replicate.

### VI. Instrumental Settings

Upper electrode:	3954
Lower electrode:	4006
Sample Charge:	15 mg.
Wavelength ( $\text{A}^\circ$ )	Ultraviolet - 2nd order
	A 5000-6000
	B 6000-7000
DC Current (Amp.):	18
Exposure (sec.):	120

### VII. Quantitation

The photographic plate generated is interpreted at the wavelength unique to the element of interest. Calibration/Standard curves are plotted by concentration (wt%) versus the logarithms of the optical density of the measured line.

The element concentration in the original sample is determined by dividing the quantitative result obtained from the photographic plate by the concentration factor (CF).

$$\text{CF} = \text{original sample wt./g. ash} + \text{Ga}_2\text{O}_3$$