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® and Pemulen™* products manufactured in benzene or ethyl acetate/cyclohexane after suitable ashing and combining with Ga₂O₃.

II. Apparatus
2. NSL Model 110-90 Multisource.
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 (Ga₂O₃), Electronic Grade, 5 9s Pure, Eagle Picher.
2. Redistilled Nitric Acid (HNO₃), Baker.
3. Reagent Grade Sulfuric Acid (H₂SO₄), 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 H₂SO₄ and 0.5 ml HNO₃ 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 Ga₂O₃ (30 mg min.).
The inorganic ash+Ga₂O₃ is returned to the fume hood and a slurry is made in the ceramic crucible by adding 0.5 ml of HNO₃. 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 Ga₂O₃ + 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.
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 (A):
- 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 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).

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

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® polymerized in ethyl acetate. Coprecipitation of an added or constituent metal is routinely employed.

II. Apparatus For Quantitation
(a) B&L Dual Grating Emission Spectrometer (or equiv.)
(b) NSL Model 110-90 Multisource (or equiv.)
(c) Baird Atomic Micro Densitometer (or equiv.)

III. Sample Preparation (Chemical)
(a) 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.

(b) 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 agalagmator 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.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelengths (Å) Evaluated</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>2780.2, 2860.5</td>
</tr>
<tr>
<td>Bi</td>
<td>3067.7, 2898.0, 2938.4</td>
</tr>
<tr>
<td>Cd</td>
<td>3466.2, 3404.6, 2980.6</td>
</tr>
<tr>
<td>Pb</td>
<td>2833.1, 2663.2, 2802.0</td>
</tr>
<tr>
<td>Sb</td>
<td>2528.5, 2877.9, 2598.1</td>
</tr>
<tr>
<td>Sn</td>
<td>3175.1, 3262.3, 2840.0, 2863.3</td>
</tr>
<tr>
<td>Ag</td>
<td>3280.7, 3382.9</td>
</tr>
</tbody>
</table>

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 µg of mercury.

VII. Calculations

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

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).

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