
**7.01 DETERMINATION OF LEAD AND ARSENIC IN CERTIFIABLE
COLOR ADDITIVES AND COLOR ADDITIVE LAKES
BY X-RAY FLUORESCENCE SPECTROMETRY**

Section 1. Introduction

21 CFR Parts 74 and 82 specify the maximum allowable amounts of lead and arsenic in certifiable color additives and their lakes. X-ray fluorescence spectrometry is used as a screening method for determining the amounts of these impurities. In this method, a sample is pressed into a pellet and subjected to radiation from a rhodium end-windowed X-ray tube. The radiation causes the elements present to fluoresce, or emit X-rays with wavelengths characteristic of those elements. A Soller slit selects a parallel beam of the fluorescence radiation and directs it to an analyzer crystal. The analyzer crystal diffracts each wavelength of the fluorescence radiation at a different angle. The diffracted radiation goes through a second Soller slit and into the detector, where the intensity of each wavelength is measured by a gas-flow proportional counter (for long to intermediate wavelengths) and a scintillation counter (for short wavelengths).

Each wavelength in the beam is diffracted at a different angle according to the Bragg relationship:

$$n\lambda = 2d \sin\theta$$

where

n = order of reflection

λ = wavelength

d = analyzer crystal lattice spacing

θ = angle of diffraction

Each element gives one or more peaks at characteristic angles that are determined by the analyzer crystal lattice plane spacing (d) and the wavelength(s) emitted. The peak intensities are calibrated using external standards prepared in a matrix similar to the sample.

Section 2. Apparatus

- A. **X-ray fluorescence spectrometer** - Siemens, model SRS-300AS
- rhodium end-windowed X-ray tube with 125- μm thick beryllium window
- B. **Computer**, with MPA board, EGA monitor - IBM/AT
- C. **Computer programs**
"MATRIX10" - developed for this method
"MATRIX12" - developed for this method
"SPECTRA/AT" - Siemens on-line measurement program
- D. **Printers**, color jet and dot matrix
- E. **Cooling water supply**, minimum 3 L/min at 4.5 Bar, maximum 20°C
- F. **Air compressor**, minimum 20 L/min at 4.5 to 10 Bar - Air Techniques, Inc.
- G. **Tapered pellet cups**, aluminum - Chemplex Industries, Inc., Cat. No. 505
- H. **Disposable XRF sample cups**, polyethylene thermoplastic - Chemplex Industries, Inc.,
Cat. No. 1540
- I. **X-ray polypropylene film**, 6.3 μm - Chemplex Industries, Inc., Cat. No. 430
- J. **Microporous film**, polypropylene - Chemplex Industries, Inc., Cat. No. 325
- K. **Sample cup holders with 23-mm diameter graphite masks** - Siemens, Cat. No. C79298-
A3141-B86
- L. **Sample tray**
- M. **Analytical balance**, accurate to 0.1 mg
- N. **Vacuum oven** with pump and gauge
- O. **Magnetic stirrer-hot plate**
- P. **Magnetic stirbar**, Teflon coated, 1 inch
- Q. **Microliter pipets**, adjustable volume, sizes 200 and 1000 μL
- R. **Hydraulic press with 30 mm tungsten carbide press tool** - Herzog, model HTP-20
- S. **Regulator for P10 gas**

Section 3. Reagents

- A. Nitric acid, concentrated, ultrapure - Baker, Cat. No. 6901-05
- B. Water, ultrapure - Ionics
- C. P-10 compressed gas (10% methane, 90% argon), ultra-high purity
- D. Standards

Lead in 10% nitric acid solution, 10.00 mg/mL - National Institute of Standards and Technology, Standard Reference Material 3128

Arsenic in 15% hydrochloric acid solution, 10.00 mg/mL - National Institute of Standards and Technology, Standard Reference Material 3103

Steel High Carbon (modified) - National Institute of Standards and Technology, Standard Reference Material 1264a

- E. Matrix color additive (for preparation of calibration standards and blanks) - FD&C Yellow No. 6, certified free of lead and arsenic

Section 4. Preparation of Glassware

Soak all glassware to be used in a 10% nitric acid bath for at least two hours to remove trace metals. Rinse thoroughly with water.

Section 5. Standard Solutions

- A. Lead, 1000 ppm (Pb stock solution)

Add ca 75 mL of water to a 100 mL volumetric flask. Using volumetric pipets, transfer 1 mL of nitric acid and 10 mL of the standard lead solution to the flask. Dilute to volume with water, stopper, and shake to mix. Use until consumed.

- B. Arsenic, 1000 ppm (As stock solution)

Add ca 75 mL of water to a 100 mL volumetric flask. Using volumetric pipets, transfer 1 mL of nitric acid and 10 mL of the standard arsenic solution to the flask. Dilute to volume with water, stopper, and shake to mix. Use until consumed.

Section 6. Procedure

A. Preparation of samples

To minimize dust contamination from the color additives, prepare the samples in a separate room adjacent to the X-ray spectrometer instrument room. Pass the prepared samples on trays through an air lock to the instrument room for analysis.

Prepare a disposable sample cup with a 6.3 μm polypropylene film front window. Using a spatula, place a sample in the automatic press tool mold. Take a sufficient amount of sample to prepare a ca 3 mm-thick color additive sample pellet or a ca 6 mm-thick color additive lake sample pellet. Place the press die in the mold on top of the sample. Apply ca 50 kN of pressure for 3 sec. Remove the die and remove the pellet. Handle the pellet by its curved edge only. Light matrices sometimes allow X-rays to pass through the pellet and consequently excite fluorescence from the lead in the sample chamber. To avoid this, place two or three aluminum tapered pellet cups on the back of the pellet.

Carefully place the pellet in the sample cup. Cover the other end of the cup with microporous film. Write the sample number and color additive type on the microporous film. Place the sample cup in a sample cup holder and store in a sample tray.

B. Preparation of the matrix

Using a top-loading balance, weigh ca 500 g of the matrix into a 600 mL beaker. Cover with a watch glass. Dry in a vacuum oven at 110 °C, 20 psi, for ca 2 hr or overnight. Transfer to a desiccator and allow to cool to room temperature (ca 1 hr).

C. Preparation of calibration standards

Weigh fourteen 30.00 g (± 0.01 g) portions of the matrix into separate 600 mL beakers. Add ca 300 mL of water to each beaker and stir until each sample dissolves. Using micropipets, transfer aliquots of the Pb stock solution as listed in Table 7.01/1 to the first seven beakers and transfer aliquots of the As stock solution as listed in Table 7.01/1 to the remaining seven beakers.

Add a stirbar to each beaker and cover with a watch glass. Using a stirrer-hot plate, heat to boiling with stirring, and boil until the solid is nearly dry. Dry overnight in a vacuum oven at 110 °C, 20 psi. Transfer to a desiccator and allow to cool to room temperature (ca 1 hr).

Using a stainless steel spatula, transfer each sample of dried material to a large mortar. Remove the stirbar. Grind the sample thoroughly. Replace the ground sample in the 600 mL beaker. Cover the beaker with a watch glass and store it in a desiccator. Use to prepare a pellet as described in Section 6-A. Retain a portion of the solid used to make the pellet for analysis of lead or arsenic content by atomic absorption spectrometry.

TABLE 7.01/1 Analyte Concentration in Lead and Arsenic Calibration Samples

Aliquot of Pb or As Stock Solution (μ L)	Concentration of Lead or Arsenic (ppm)
0	blank
30	1
90	3
150	5
300	10
1500	50
3000	100

D. X-ray system parameters

Two computer programs, MATRIX10 and MATRIX12, are used for the analyses of lead and arsenic in color additive samples. MATRIX10 is used for the analyses of lead and arsenic in samples that do not contain bromine. MATRIX12 is used for the analyses of lead in color additives that contain bromine (D&C Orange No. 5, D&C Red No. 21, D&C Red No. 22, D&C Red No. 27, and D&C Red No. 28).

Bromine produces a large peak that overlaps with the Pb $L\beta_1$ peak, so that the Pb $L\alpha$ peak (which overlaps with the As $K\alpha_{1,2}$ peak) is measured instead. Thus, lead is measured as arsenic and arsenic cannot be measured independently in those samples.

(1) Parameters for lead in MATRIX10

Analytical line: $L\beta_1$ 28.195° 2 θ

Background measurement positions: 27.504° and 28.885° 2 θ

Wavelength: 0.9830 Å

Mask: 23 mm

Counting time: 100 sec

Analyzer crystal: LiF(100)

X-ray tube voltage and current: 60 kV, 40 mA

Collimator: fine

Filter: none

Detectors: flow counter, pulse height window minimum 0.9, maximum 1.2; scintillation counter, pulse height window minimum 0.5, maximum 1.5

Detector gas: P10

Intensity model: peak minus background

Correction model: intensity

Mode: air

Dead-time correction: on

Rotation: on

(2) Parameters for arsenic in MATRIX10

Analytical line: $K\alpha_{1,2}$ 33.991° 2 θ

Background measurement positions: 33.491° and 34.491° 2 θ

Wavelength: 1.1774 Å

Mask: 23 mm

Counting time: 100 sec

Analyzer crystal: LiF(100)

X-ray tube voltage and current: 60 kV, 40 mA

Collimator: fine

Filter: none

Detectors: flow counter, pulse height window minimum 0.9, maximum 1.2; scintillation counter, pulse height window minimum 0.5, maximum 1.5

Detector gas: P10

Intensity model: peak minus background with Pb $L\beta_1$ line overlap correction

Correction model: intensity

Mode: air

Dead-time correction: on

Rotation: on

(3) Parameters for lead in MATRIX12

Element: Pb (as As)

Analytical line: As $K\alpha_{1,2}$ and Pb $L\alpha$ $33.991^\circ 2\theta$

Background measurement positions: 33.491° and $34.491^\circ 2\theta$

Wavelength: 1.1774 Å

All other parameters are the same as those for lead in MATRIX10.

E. Determination

The X-ray spectrometer has potential radiation and high-voltage electric shock hazards and must be used only by suitably trained personnel.

Load the autosampler with the samples from the sample tray as follows: Place a lead cylinder sample in position 1 (this is analyzed to make sure the autosampler is functioning correctly). Place the SRM 1264a standard in position 2 (this is analyzed to monitor instrumental drift). Place a blank sample in position 3. Place the color additive and color additive lake samples in the next positions. Place the

10 ppm lead and 10 ppm arsenic calibration standards in the last two positions (these are analyzed as unknowns).

Enter the following information into an X-ray analysis sheet (XAS):

1. Sample number
2. Type of sample
3. Position number in autosampler
4. Matrix program: MATRIX10 or MATRIX12
5. Mode of analysis: RE = reference sample mode (for the SRM 1264a standard); UN = unknown sample mode (for all other samples)

At the main menu of the SPECTRA/AT software program SPECTRA, place the cursor on MEASUREMENT OPERATIONS and press the ENTER key. Enter the information from the XAS plus the following information into the sample list. Table 7.01/2 shows how all of the data should be entered.

6. Repeat factor (usually 0)
7. Time scale factor (1.00)

Following the data entry, press the F10 key to begin the analytical run. To obtain a printout of the results immediately after each sample has been analyzed, place the cursor on VERIFY SRS STATUS and press the ENTER key. Otherwise the printout will occur after all the samples have been measured.

Section 7. Calculations

A. Calibrations

The programs MATRIX10 and MATRIX12 contain calibration curves that are used for the analyses of lead and arsenic. Corrections for instrumental drift are made at the beginning of each analytical run by measuring the SRM 1264a standard, using the changes in intensity of the standard to recalibrate the

instrument. The calibrations are checked at the end of each run by measuring lead and arsenic calibration standards as unknowns. Their results should be within ± 2 ppm. If not, the instrument should be recalibrated.

B. Analyte concentrations in samples

The programs MATRIX10 and MATRIX12 automatically calculate the amounts of lead and arsenic present in each unknown sample from calibration tables in the programs and from the intensities of the analyzed calibration standards. Record the results in the appropriate notebook.

If the lead or arsenic content in a sample is found to be above the specification level, prepare and analyze a second, thicker pellet. If the second pellet also contains a high amount of lead or arsenic, scan the pellet to determine if any other factor is present that contributes to the high result. If none is found, confirm the high result by atomic absorption spectrometry.

Table 7.01/2 SPECTRA/AT On-line Measurement Program

Sample and/or file name	Pos	Program file name	Mod	Re	T.S.
PB	1	MATRIX10.QAN	UN	0	1.00
SRM1264A	2	MATRIX10.QAN	RE	0	1.00
BLANK	3	MATRIX10.QAN	UN	0	1.00
Y6-92-9966	4	MATRIX10.QAN	UN	0	1.00
R40-93-0044	5	MATRIX10.QAN	UN	0	1.00
PB10	6	MATRIX10.QAN	UN	0	1.00
AS10	7	MATRIX10.QAN	UN	0	1.00