Mercury Determination in Certifiable Color Additives Using Thermal Decomposition Amalgamation and Atomic Absorption Spectrometric Analysis

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Abstract

Background: Most color additives requiring FDA batch certification are analyzed by x-ray fluorescence spectrometry (XRF). However, sensitivity for mercury (Hg) is too low in some color additives.
Purpose: The aim of this study was to evaluate the effectiveness of thermal decomposition amalgamation-atomic absorption spectrometric (TDA-AAS) for analysis of Hg in the various types of certifiable color additives as part of FDA's color certification program.
Methodology: Tests were performed to optimize conditions and test reliability of Hg determinations at and below the CFR specification limit of 1 mg/kg.
Results: Factors that affected results were appropriateness of the calibration procedure and condition of the catalyst, which was sample matrix dependent. Regular quality checks using certified reference materials and in-house matrix-matched check standards are essential.
Conclusions: TDA-AAS can be used for determining Hg concentrations at and below the CFR specification limit in all color additives [1], including those that are difficult to analyze by XRF. However, it is less efficient for color additives containing nitrogen, sulfur, and halogens, which quickly deteriorate the catalyst. Color additives containing barium sulfate that are difficult to analyze by other techniques are well suited for TDA-AAS.

Introduction

- Color additives requiring FDA batch certification are analyzed for mercury (Hg) by x-ray fluorescence spectrometry (XRF) [2], but some color additives present difficulties.
- Barium sulfate ($BaSO_4$) in D&C Red No. 6 and 7 lakes limits sensitivity of XRF for Hg.
- Bromine (Br) in D&C Red Nos. 21, 22, 27, and 28 and iodine (I) in FD&C Red No. 3 and D&C Orange No. 5 interfere with determination of traces of Hg by XRF.
- Inductively coupled plasma-mass spectrometry (ICP-MS) may be used as an alternative but is labor-intensive and has issues because of Hg's high ionization potential, and it's potential to adsorb and/or volatilize.
- Therefore, a thermal decomposition amalgamation-atomic absorption spectrometric analysis (TDA-AAS) method for determining trace levels of Hg in all color additives, including those that are difficult to analyze by other techniques, was developed.
- However, many color additives contain nitrogen (N) and sulfur (S) and several contain chlorine (Cl), Br, and I, which upon combustion produce compounds that may interfere with TDA-AAS determination of Hg.
- The aim of this study was to evaluate the effectiveness of TDA-AAS for analysis of Hg in the various certifiable color additive matrices.

Materials and Methods

Apparatus

- TDA-AAS Hg analyzer - DMA-80 evo, Milestone Scientific
- Combustion boats, quartz and nickel

Reagents

- Color additives (from various manufacturers)
- Spectrometric standard (Hg, 1000 mg/L)
- Reference materials
  - SRM 2703 (sediment, 0.5 mg/kg Hg, 0.7 mg min)
  - In-house standard (FD&C Yellow No. 6, Y6, 1 mg/kg)
- Diluting solution (DS): 1.0% HCl in water

Instrument parameters

- Optimized parameters are shown in **Table 1**.

Calibration

- Standard solutions: Serially-diluted spectrometric standard to make 100 mg/L, 10 mg/L, 1.0 mg/L, and 0.1 mg/L Hg solutions.
- Calibration curves were in two ranges: 0-25 ng (quadratic fit), and 25-300 ng (linear fit)

Quality assurance

Reference materials are needed to monitor instrument performance
Reference materials used:

- SRM 2703 (chosen for small sample size)
- In-house Y6 standard (chosen for sample matrix similarity)

Other reference materials evaluated, but not employed:

- DORM-4 (not used due to odor and large sample size)
- SRM 1632e (not used due to large sample size)

Sensitivity test

- Samples tested
  - Ten empty combustion boats fortified with 0.1 mg/L Hg
  - Ten 0.010 g portions of Y6 in boats, fortified with 0.1 mg/L Hg
- Full Hg recoveries (with or without color additive)
- Standard deviations were used to estimate
  - Detection limit of 0.002 mg/kg (0.002 ppm) Hg (in color additives)
  - Quantitation limit of 0.006 mg/kg (0.006 ppm) Hg
  - Since 10 measurements were taken on one day, with one catalyst, using one calibration; a conservative estimate is 10x these values
  - Thus, quantitation limit was 0.06 mg/kg (0.06 ppm) Hg
- Substantially better than XRF (~ 1 ppm); and
- Equal or better than ICP-MS (~0.1 ppm)

Precision

Precision was controlled at 20%; catalyst was replaced, and instrument recalibrated when reference materials deviated by more than 20%

Color additive testing

- For several months, all color additives submitted to the FDA for certification testing were routinely analyzed for Hg by TDA-AAS.
- Most color additive samples analyzed routinely by TDA-AAS had trace or no detectable Hg.
- SRM 2703 and in-house Y6 reference standards were analyzed after every 20 samples and at the beginning and end of each run.
- Every 20th sample was fortified in duplicate with 10 µL of 0.1 mg/kg (1 ng Hg, 0.1 ppm in the color additive) and evaluated for its relative standard deviation (RSD).
- Results were discarded for samples where RSDs exceeded 10%, or when reference samples were out of control limits, and corrective actions were taken before re-analysis.
- When all color additives were analyzed routinely, the instrument needed frequent (biweekly) catalyst replacements and recalibrations, severely reducing productivity.
- When only those samples that were not more easily analyzed by XRF were analyzed by TDA-AAS, catalyst life was extended to five months.

Table 1. TDA-AAS method conditions for color additives

Parameter	Value(s)
Sample size	0.010 g
Ramp time and drying temperature	10 s 200 °C
Maximum starting temperature	250°C
Drying hold time and temperature	30 s 200 °C
Ramp time and combustion temperature	90 s 750 °C
Combustion hold time and temperature	90 s 750 °C
Purge time	60 s
Amalgamator heating time	12 s
Signal recording time	30 s

Results and Discussion

Testing of specific samples

Representatives of different dye classes were analyzed in duplicate with and without fortification at 1 ng Hg (0.1 ppm in the color additive)

Dye class	Representative color additive	Potential catalyst degrader
Azo	FD&C Red No. 40	N and S
Indigoid	FD&C Blue No. 2	N and S
Pyrazolone	FD&C Yellow No. 5	N and S
Quinoline	D&C Yellow No. 10	N and S
Anthraquinone	Ext. D&C Violet No. 2	N and S
Triphenylmethane	FD&C Blue No. 1	N and S
Xanthene	D&C Red Nos. 21 and 22	Br
Xanthene	D&C Red Nos. 27 and 28	Cl and Br
Xanthene	FD&C Red No. 3	I

Full recoveries were obtained by TDA-AAS, within 20% and usually within 10%.

- Samples that produced values over the 1 mg/kg (1 ppm) Hg were also analyzed by XRF and ICP-MS for comparison (see **Table 2**).
- Each of the methods (TDA-AAS, XRF, and ICP-MS) has limitations.
  - TDA-AAS is precision controlled (larger estimated errors)
  - N, S, Cl, Br, and I gradually degrade the TDA-AAS catalyst
  - TDA-AAS and ICP-MS use small portions (homogeneity issues)
  - ICP-MS loses Hg by volatilization and/or adsorption, and Hg is difficult to ionize; also, ICP-MS is very labor intensive
  - XRF is less sensitive, especially when there are interfering elements (Ba in D&C Red No. 6 Ba lake or Br in D&C Red Nos. 21, 22, 27, 28, and I in FD&C Red No. 3)

Within these parameters, the values in Table 2 agree.

Performance

- The TDA-AAS method has advantages over methods requiring sample pretreatment.
- However, efficiency is reduced for samples containing nitrogen, sulfur, or halogens.
- Carry-over lengthens analysis and requires monitoring by measuring blanks.
- The TDA-AAS method works satisfactorily for samples which are difficult to analyze by other techniques, e.g., those with Br and I, and works very well for color additive lakes containing Ba.

Table 2. Hg values (mg/kg) for samples exceeding 1.0 mg/kg by three techniques. Values are averages of three replicates. Estimated errors: ± 1.0 mg/kg Hg for TDA-AAS and XRF, ± 0.5 mg/kg Hg for ICP-MS

	TDA-AAS	XRF	ICP-MS
FD&C Blue No. 1 a	4.6	4.6	4.2
FD&C Blue No. 1 b	4.3	4.7	3.8
FD&C Blue No. 1 c	4.4	4.7	3.8
FD&C Blue No. 2 a	6.1	5.5	6.2
FD&C Blue No. 2 b	6.6	5.2	6.8
FD&C Blue No. 2 c	1.1	1.2	1.1
FD&C Yellow No. 6 a	3.3	3.0	2.8
FD&C Yellow No. 6 b	3.2	2.8	2.8
FD&C Yellow No. 6 c	4.2	3.7	3.7
FD&C Yellow No. 6 d	4.3	3.8	3.8
FD&C Yellow No. 6 e	3.5	3.2	3.1
FD&C Yellow No. 6 f	4.0	3.9	3.6
FD&C Yellow No. 6 g	3.1	2.4	2.8

Conclusions

- The TDA-AAS technique can detect very low levels of Hg in certifiable color additives.
- The technique is accurate and quick for individual samples.
- N, S, and halogen components of color additives can degrade the TDA-AAS catalyst and reduce efficiency, but the technique is still effective.
- The technique is most valuable to FDA for the analysis of color additive lakes containing Ba.

References

1. Code of Federal Regulations (2020) Title 21, U.S. Government Printing Office, Washington, DC, Parts 73, 74, and 82
2. N. M. Hepp and I. C. James, *X-Ray Spectrom.* 2016, **45**, 330–338