TECHNICAL NOTE

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Thin-Layer Chromatography of Metallic Cations

ABSTRACT: Two silica gel thin-layer chromatographic systems are described that are capable of distinguishing 18 common metallic cations by mobility and color development with one of three visualization reagents. Two groups of cations arise from this ion mobility: a "fast" group containing molybdenum, iron, antimony, tin, mercury, arsenic, cadmium, zinc, cobalt, copper, manganese, and bismuth, and a "slow" group containing chromium, aluminum, magnesium, nickel, calcium, and lead. The analytical method can be applied to comparing and identifying inorganic cations in small samples of evidential materials.

KEY WORDS: criminalistics, chromatographic analysis, cations

Thin-layer chromatography (TLC) is worthy of a number of analytical applications and offers great potential in simultaneously separating and identifying mixtures of various metallic ions [1,2]. This rapid, easily mastered technique can greatly aid in comparisons of the inorganic cations present in materials such as alloys or paints [3].

An examination of various solvent mixtures has identified two TLC systems that, when coupled with the reactions of designated chemical visualization agents, are capable of separating and distinguishing 18 inorganic elements commonly encountered in forensic analysis.

Even though evaluation by this method requires pyrolytic destruction of organic paint vehicles, a tube technique [4] can be used that collects the organic pyrolyzate for further analysis and results in complementary organic and inorganic sample preparation. The procedure is applicable to comparative analysis and provides qualitative cation identification; quantitative data have not been developed since some of the visualized zones fade.

Materials and Reagents

Certified Fisher atomic absorption standard reference solutions of the following elements, containing 1 mg of cation per millilitre, were used as standards for thin-layer analysis: molybdenum, iron, antimony, tin, mercury, arsenic, cadmium, zinc, cobalt, copper, manganese, bismuth, aluminum, magnesium, nickel, lead, and calcium. A chromium standard was prepared from chromium trioxide in aqua regia and diluted to 1 mg/mL

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chromium. Titanium dioxide and zirconium dioxide are insoluble in aqua regia and consequently are not identifiable by this method.

Additionally, samples of each of the following compounds were dissolved in aqua regia and used as reference cation solutions: ferric chloride, antimony trichloride, calcium oxide, bismuth nitrate, nickel monoxide, barium oxide, lead carbonate, stannous chloride, red mercuric oxide, arsenic trioxide, aluminum chloride, magnesium oxide, cupric oxide, cobaltous chloride, magnesium dioxide, cadmium chloride, chromium trioxide, and zinc oxide. All reagent acids, solvents, or visualization agents were Fisher-certified American Chemical Society grade with the exception of Fisher "purified" amyl acetate, which was used as supplied.

The dithizone visualization reagent (Method I) was prepared as a 0.1% diphenyl-thiocarbazone solution in carbon tetrachloride. The oxine reagent (Method II) is a 0.5% solution of 8-hydroxyquinoline in isopropanol; this spray reagent is followed by an over-spray of concentrated aqueous ammonia.

Lead is visualized by overspraying the lower portion of the System II plate with an aqueous solution of sodium rhodizonate, followed by 1% aqueous hydrochloric acid.

The following commercial silica gel thin-layer chromatographic (TLC) sheets were compared in this study: Eastman Chromagram sheet No. 6060, 13181 silica gel with fluorescent indicator, Eastman Kodak Co., Rochester, N.Y.; Schleicher & Schuell F 1500 silica gel sheets, Schleicher & Schuell, Keene, N.H.; and EM Nano-HP-TLC silica gel 60 plates, catalog No. 5631, 10 by 10 cm, available through E. M. Laboratories Inc., Elmsford, N.Y.

Method

For organic-inorganic mixtures, a disposable 230-mm (9-in.) Fisher brand pasteur pipet is modified into a pyrolysis tube by scoring the body 25 mm (1 in.) below the neck, breaking the pipet, and discarding the large diameter (unnecked) portion. After a weighed sample of from 1 to 3 mg of material (as paint) is introduced into the shoulder of a modified pipet, the large diameter end is heated with a propane torch, allowed to melt, and sealed. While still glowing (and in the flame) the tube is inverted and the (paint) sample forced to fall onto the hot glass bottom. Pyrolysis is usually rapid, and the tube is removed from the flame after about 10 s. The open capillary tip is then rapidly sealed in the burner flame and the sample allowed to cool; all collectible pyrolized volatiles are condensed in the neck of the apparatus.

When cool, the large diameter end of the pyrolysis tube is scored near the center and broken. The nonvolatile, inorganic residue remaining in the tube bottom is (partially) dissolved in two drops of freshly prepared aqua regia (one drop concentrated nitric acid/three drops concentrated hydrochloric acid) and about 15 μL of this solution is spotted 2 cm from the base of each of two thin-layer sheets and allowed to air-dry. Metallic alloys or inorganic substances can usually be directly dissolved in aqua regia and spotted on the TLC sheet.

Thin-layer chromatography is carried out concurrently with unknown samples and comparative standard mixtures of known cations. Sealed equilibrated glass tanks, each containing a solvent layer about 1 cm deep, are used in developments. For best results these solvents must age overnight before use; failure to age the solvents creates variable mobilities with some cations (a phenomenon easily demonstrated with cobalt and copper).

The samples are run in each of the following solvent systems.:

System I is a single 18-cm development in a solvent composed of methyl isobutyl ketone, amyl acetate, and concentrated hydrochloric acid (60:35:8). This is the "fast" cation system.

System II is a single 15-cm development in a solvent composed of methyl isobutyl ketone, amyl acetate, methanol, and concentrated hydrochloric acid (4:1:1:2). This is the "slow" cation system.

Standard cation mixtures include (a) (fast) molybdenum, tin, cadmium, and copper; (b) (fast) iron, mercury, zinc, and manganese; (c) (fast) antimony, arsenic, cobalt, and bismuth; (d) (slow) chromium, magnesium, and lead; and (e) (slow) aluminum, nickel, and calcium.

The developed chromatograms are air-dried and visualized. The System I plate is sprayed with the dithizone reagent (Method I) and may be followed by fuming with ammonia. The System II plate is sprayed with oxine reagent followed by a spray of aqueous ammonia (Method II). While the cations of System I all form visible colored zones, some System II cations are visualized as fluorescent areas under long-wave ultraviolet light.

Results

The results of 18 standard cation migration distances and visualized color patterns are summarized in Table 1. Each of these values was determined by using 5 μg of metallic ion; distortions in migration distances were not noted in mixtures of ions in this concentration range. In general, 2 μg of each metallic ion is not below the limit of detectability.

Of the thin-layer sheets tested, the Schleicher & Schuell F 1500 silica gel material proved most satisfactory. These sheets developed with a uniform solvent front in a rapid discriminating fashion. The Eastman sheets produced an irregular solvent front and ran slowly while the Nano-HP-TLC plates (10 cm on an edge) did not provide as fine a resolution as did the Schleicher & Schuell sheets, possibly because of the short migration path.

Decreasing the ketone concentration slows down metallic ions in the TLC scheme (decreases R_f); also, a small change in the acid content in System I can produce large changes in ion mobility. The use of acetone and ethyl acetate, with hydrochloric acid, gave poorer separation of cations than did the use of System I.

TABLE 1—*Summary of results.*

Cation	TLC System	R_f	Color by Visualization Method I	Color by Visualization Method II
Molybdenum (II)	I (fast)	0.86	pink	yellow
Iron (III)	I	0.82	yellow[a]	black
Antimony (III)	I	0.76	orange	none
Tin (II)	I	0.74	red	yellow fluorescence
Mercury (II)	I	0.54	pink	yellow
Arsenic (III)	I	0.46	yellow	none
Cadmium (II)	I	0.42	purple	yellow fluorescence
Zinc (II)	I	0.38	red	yellow fluorescence
Cobalt (II)	I	0.33	blue[a]	purple fluorescence
Copper (II)	I	0.30	yellow-green[a]	purple fluorescence
Manganese (II)	I	0.16	pink	purple fluorescence
Bismuth (III)	I	0.14	red	yellow
Chromium (III)	II (slow)	0.55	. . .	green;[a] dark ultraviolet
Aluminum (III)	II	0.50	. . .	yellow fluorescence
Magnesium (II)	II	0.46	. . .	bright yellow fluorescence
Bismuth (III)	II	0.45	. . .	yellow
Nickel (II)	II	0.40	. . .	green;[a] purple ultraviolet
Calcium (II)	II	0.35	. . .	yellow fluorescence
Lead (II)	II	0.30	. . .	red with sodium rhodizonate reagent; hydrochloric acid

[a] Visible before application of spray reagent.

Overnight equilibration of the solvents was found to be useful, and although standing for several days produced decomposition (color change) this did not seem to adversely affect cation migration or separation.

The collected data show that two groups of cations seem to emerge from these systems: the "fast group" containing twelve elements and the "slow group" containing six elements (Table 1).

Discussion

The mobility of metallic inorganic substances in TLC depends primarily on the oxidation state, the bound ligands, and the solvation of the cation. For a valid analytical comparison, identical bound ligands must surround a cation of a given oxidation state. By bringing a cation into a strongly acid, strongly oxidative medium, the cation achieves a stable, high oxidation state, thus eliminating problems involving amphoteric characteristics.

Chlorides were chosen for their ease of formation and general solubility. The properties of these metal halides are complex and determined by a number of factors including coordination number and formation of covalent as well as ionic and anionic complexes; a detailed explanation of the ion-solvent bonds and complexes that exist with each of the metallic cations used is beyond the scope of this communication [5].

The formation of a high oxidation state cation, with fairly uniform ligand complexation, is conveniently accomplished by dissolution of a sample in aqua regia, an oxidizing medium that will destroy many organic substances and simultaneously solubilize most common metal cations. This procedure has been incorporated into various analytical methods for metallic elements including Gutzeit's analytical scheme [6]. When the procedure is carried out on samples in a side-by-side fashion, oxidation states for all common cations should be comparable, and chloride and water probably occupy many of the available ligand sights, thereby permitting meaningful TLC analysis.

Since many important inorganic cations, anticipated in paint pigments [3], paint driers [3], and metallic alloys, are detected and visualized by TLC, the simple method presented here offers a rapid screening procedure for qualitative identification or comparisons. This method is not recommended as a substitute for quantitative techniques but is suggested as a comparison for selecting those specimens worthy of further evaluation. This method may be usefully extended to the analysis of bomb debris, soil, and other evidential material.

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