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A Scientific Study of Pencil Lead Components

The term "lead" pencil is a misnomer in that the pencil contains no lead but rather is composed of three primary ingredients in varying proportions: graphites, clays, and waxes [1]. Since its introduction during the 16th century, the pencil has become the most widely used writing instrument throughout the world. Americans yearly consume over two billion pencils, with the U.S. government and Bell Telephone System being the largest purchasers. It has been reported that enough pencils are produced every year in the United States to supply every American with one pencil every 40 days. [3]

Since the pencil occupies the unique position of being the most versatile and most used writing instrument available today, the number of documents that bear some form of pencil writing is remarkable. Some of these pencilled writings, through circumstance, later come to possess evidentiary value in that they help to establish or disprove facts at issue. It is in this area that the task of identifying a particular type of pencil lead used in the execution of a specific document can assume great importance.

Historically, little scientific effort was expended on the forensic identification or differentiation of various pencil leads. A review of the literature in the field of questioned documents yielded only one article dealing with this subject [1]. A paucity of information likewise exists concerning the general composition of pencil leads, their historical and present-day methods of production, or what chemical and physical examinations can be conducted on the constituent components of pencil lead [2-6].

Kirk [2] commented, "Because of the essential simplicity of composition of the pencil lead, pencils have a very limited degree of individuality, and can not ordinarily be identified as individuals." Morland [3] has likewise concluded that "there is little individuality in the pencil itself, though the materials from which it is made are known to investigators." Osborn [4] had earlier concluded that the forensic identification of pencil leads was practically useless. He reported that "one can establish whether two writings were produced by the same lead pencil by determining the difference in hardness (due to the proportion of graphite and clay) which affects the width, character, and indentation of the stroke." He concluded, however, that "any attempt to analyze chemically an ordinary pencil stroke for the purpose of identity is practically impossible."

Hilton [5] reported that it can seldom be established that a particular pencil was used to write a document: "Identification of this nature must be based on microscopic flaws in the stroke, resulting from impurities in the graphite, and involves extensive microscopic examination combined with controlled lighting and photography. Usually, a pencil does not have sufficient individuality to permit a definite conclusion."

The most negative comment regarding the inability to distinguish pencil leads was made by Harrison [6], who reported, "Whilst pencils of different qualities make marks which are appreciably different on microscopic examination, it is impossible to determine either the make or date of production of the pencil by any examination that can be applied to the written line."

The only published article that deals specifically with developing a chemical technique to aid in differentiating among pencil leads is a 1969 article by Tholl [7], which reported that the use of thin-layer chromatographic (TLC) techniques had resulted in the success-ful fractionation of both organic and inorganic pencil pigments. Tholl determined experi-mentally that pencil components did not fractionate with the same ease or in quite the same manner as inks and that they required special extraction and development systems. He attempted to devise a simple but effective method of extracting the organic and in-organic lead substances by converting them into dissoluble products for separation analysis. Realizing the contaminating effects of paper, he likewise analyzed specimens of the paper and the developing solvent as control samples. All of his TLC procedures were designed to "fingerprint" qualitatively the metal components present in the finished lead products of the different graphite lead manufacturers.

It should be noted, however, that Tholl [7] never conducted separate analytical tests on the individual pencil components (graphites, clays, and waxes) but rather limited his analysis to samples of the finished lead products. Although the developed TLC plates did reveal some differences in R_f values for fractionated lead components, Tholl was unable to identify these components, nor did he make any effort to recover the separated compounds for further chemical analysis.

Tholl [7] admitted that his work was only an introductory effort to chemically distinguish among lead products and that "there is a need for considerable research and consolidation of test results." He further stated that the practicality of the TLC analysis of pencil leads would be realized when consistent results and standardized procedures evolved, and he characterized successful research into this field of inquiry as being of "tremendous forensic value."

Questioned document examiners have known for some time that much of the experi-mental work in their field is never published nor made available to other members of their community. In an attempt to ascertain whether any significant advances had been made since 1969 in the identification or differentiation of pencil leads, we contacted a number of directors of forensic laboratories. Edwin Alford, chief, Identification Branch, U.S. Secret Service, advised that document examiners at that agency are required to examine thousands of handwritten documents yearly in an attempt to establish authorship. The cases examined include a number of threatening letters, some of which are executed in pencil, directed against the president or other high-ranking government officials. To date all investigative inquiries regarding the type of pencil used have been answered in general and somewhat inconclusive terms.

Richard Brunnelle, director, Identification Branch, Bureau of Alcohol, Tobacco and Firearms (ATF), is confronted with Internal Revenue Service tax fraud inquiries regarding distinguishing between pencil entries found in company ledger books. Although his laboratory is responsible for the development and maintenance of the only ink identification facility in the world, chemists there have yet to attempt to differentiate among pencil lead products. This reluctance to investigate pencil leads is largely due to the reported lack of individuality among pencil products.

Both Frankie Frank of the U.S. Postal Service Laboratory and Frank Devine of the Federal Bureau of Investigation Laboratory indicated that document examiners at those agencies have as yet been unable to forensically differentiate among the various pencil lead products.

It was noted during the interviews of the laboratory directors that the only laboratory

that regularly employs the chromatographic separation technique to differentiate among questioned writing inks, typewriter inks, and stamp pad inks is the ATF Identification Branch. Dr. A. A. Cantu explained that the waxes in most pencil leads may vary sufficiently in kind and amount between manufacturers to provide a basis for identification or differentiation. He suggested the use of TLC because of its adaptability to wax products, the relative lack of complex analytical procedures, and the excellent sensitivity and optimum separation obtained with microgram amounts of sample.

Thin-layer chromatography is a method for the rapid separation of small amounts of substances to show (1) the identity of compounds, (2) the number of components, (3) the purity of the tested substances, and (4) the isolation of the constituent compounds for testing with reagents. This chemical separation technique had been adopted by various document examiners and forensic chemists for the examination of inks and other writing materials.

Cantu explained that any comprehensive attempt to exhaust TLC analytical procedures in pencil lead differentiation would require (1) ascertaining the accepted methods for separation of waxes by TLC, (2) determining the accepted methods for analyzing inorganic ions by TLC, and (3) obtaining thorough formulation information regarding the major components in pencil lead.

The purpose of this study, therefore, was to distinguish both chemically and instrumentally among the pencil leads used by the 17 major pencil manufacturers and to determine the feasibility of identifying a specific type of pencil as having been used in the execution of a questioned pencilled writing.

After samples of the various graphite, clay, and wax products had been obtained from all cooperating U.S. lead manufacturers, various analytical tests were performed on these individual components in an attempt to catalog their gross and, especially, their trace metal characteristics.

Following the individual component analysis, the same analytical procedures were applied to the various combined (finished) lead samples to include the application of TLC separation techniques for the identification and classification of individual components. The detection and sensitivity limits for these various analytical tests were determined.

The extent of interference from paper, especially those papers containing clays, resins, or other organic products as fillers or binding agents, was also tested.

Pencil Lead Manufacturing Processes

Historical Development

The word "pencil" is derived from the Latin *penicillum*, or a "painter's brush." The first pencils consisted of fine brushes of human hair or animal bristles similar in texture to an artist's camel-hair brush. When the first graphite deposits were discovered in Bavaria during the 1400s, they were called *plumbago*, which is Latin for "acting like lead," and thus the name "lead pencil," still in use today, evolved [8].

The commercial manufacture of lead pencils originated in England during the reign of Queen Elizabeth I in the 16th century, when the famous Borrowdale graphite deposit was discovered in Cumberland, England. Since the extracted graphite was of such outstanding purity, much of it was taken out in large blocks and then cut into pencil rods of desired lengths. The rods were then sawed into thin veneers and encased in either pencil cedar (wood of the Virginia cedar) forming ordinary pencils or were further refined by the action of ruby cutters to form a more rounded variety [9].

After the richer portions of the Borrowdale deposit had been depleted, attempts were made to concentrate the ore, but the material so obtained never matched the quality of the richer grades of crude graphite. In Nuremburg, Germany, pencils were made from

pulverized graphite cemented into solid blocks by means of resins, gums, glue, sulfur, and other substances. None of these products, however, equalled the superior English pencil.

Independent experimentation between 1791 and 1795 by Nicholas Jacques Conte, a French scientist, and Josef Hardmuth, of Vienna, Austria, resulted in the development of the process by which all black lead pencils are nowadays produced. The process essentially involves powdering the graphite; mixing it in varying proportions with a finely ground clay so that a thick paste results; applying extensive pressure by means of a hydraulic press until the mixture has the consistency of stiff dough; extruding the plasticized mass under pressure through a brass plunger-type device, allowing the graphite mixture to be squeezed through in continuous rods; and then heating and encasing the finished product into pencils of desired lengths. Changes in the proportions of clay and graphite allow the production of various degrees of hardness. The resultant product is a relatively homogeneous product and is less costly than the pure graphite pencil [10].

Present Methods

Modern-day methods of manufacturing pencil leads can involve as many as 125 different steps in the production process. Torok and Sallese of the Faber-Castell Co. provided the following information concerning the manufacture and composition of wooden lead pencils.

Most pencil lead is now manufactured by combining artificial graphite and clay mixtures, which are later extruded from small orifices, dried, and baked. Graphite pencils are quite different in their elemental composition from colored pencils; the former are basically ceramic products while the latter are water/plastic doughs with methyl cellulose as a binder.

Graphite is one of the three major ingredients used to make pencil leads. Faber-Castell uses only natural graphite from Ceylon because its high carbon content makes it extremely black. Refinement processes separate the graphite into microscopic particles (8 and 1 μm). Later these particles are blended to achieve the desired qualities of blackness, opacity, and strength. Clay is the second primary ingredient and can be artificially manufactured. Faber-Castell extracts of clay include a natural clay mined in Klingenberger, Germany and an artificial clay mixture made up of various amounts of Georgia kaolin and Idaho montmorillonite clays, the latter being a pure plastic clay matched to the graphite. This combined graphite/clay mixture is then blended in a special ball mill where the particles are mixed with water for several weeks; this process further refines the graphite and clay particles and provides a homogeneous blend.

After the water is separated from the blend by flocculation, the mixture is compressed and extruded through a diamond die. Small batches of the lead are then placed in ovens for firing. Over a 7-h period heat is gradually increased to more than 1000°C and held for 4 h and then, just as gradually, the temperature is reduced. The key element is firing the clay into a ceramic state without affecting the graphite. The next step for the lead is a pressurized bath in special hot waxes. There are several types of waxes available in various combinations including stearic acid, tallow wax, and Japan wax. Approximately 10% by weight is absorbed by the graphite and the wax penetrates the microcellular structure.

As a line of pencil writing is drawn, the organized particles overlap like shingles on a roof. This process creates multiple layers of graphite deposits held intact by the waxes, thereby making the drawing smooth and dustless.

The amount of clay governs the hardness of the lead. There are usually 20 degrees of textures ranging from 8B (the softest) to 10H (the hardest), with intermediate gradations HB and F. Some manufacturers number their business pencils instead of designating the hardness in letters, and thus a #2 is the equivalent of an HB, a #2½ an F, and a #3 an H. As many as 63 different firms in the United States have manufactured mechanical pencils, with the leads being supplied mostly by the makers of the wooden pencils.

Georgia kaolin clay (the major clay component for Faber-Castell pencil leads) has been determined through mass spectrometry to have 94 trace materials at the part per million level, including aluminum oxide, silicon oxide, titanium dioxide, ferrous oxide, and calcium and magnesium oxides. The graphite compound used by Faber-Castell is 97% pure carbon with a variety of contaminating compounds comprising the remaining 3%.

According to the Pencil Makers Assocation, modern American pencils are made up of 40 different raw materials from 28 different countries. Nearly 1500 registered trademarks are listed with the Association, along with insignias, colors, names, and lead sizes. Most of these pencils are made by 17 American manufacturers, employing over 5000 people in 32 plants. Today the United States leads the world in pencil production and in 1973 manufactured 2½ billion pencils (Footnote 3).

Materials and Methods

Separation Methods for Waxes

Simple lipids are esters of fatty acids and alcohols. This class is further divided into two subgroups, the triglycerides (natural fats) and the waxes. As previously mentioned, waxes are naturally occurring esters of alcohols (other than glycerol) and fatty acids. The alcohols are of a high molecular weight and generally not highly unsaturated [11].

More than 30 years ago several chemists showed that lipids could be eluted as classes of compounds in fractions from an absorption column by applying various solvents of different polarities ("Elutropic Series"). It was subsequently determined that mixtures of petroleum hydrocarbons and diethyl ether in varying ratios could be used instead of mixtures of individual solvents. According to Stahl et al [12], fats, oils, waxes, and other natural lipids can be separated by absorption TLC on silica gel according to the classes of compounds. Reverse-phase partition chromatography has also been used for separating lipids according to the classes of compounds.

Stahl et al [12] have stated that silica gel is the most convenient and widely used of all the absorbents utilized in TLC lipid separation techniques. The choice of solvents depends upon the polarities of the compounds of the lipid mixture and on the desired separation. For the separation of hydrocarbon compounds and alkyl esters, Stahl et al recommended mixtures of petroleum hydrocarbon with 1 to 5% benzene or diethyl ether. For TLC separation of lipid mixtures containing free fatty acids, they recommended this solvent with 1 to 2% glacial acetic acid to avoid "tailing" or streaking effects. The system of petroleum hydrocarbon/diethyl ether/acetic acid (90:10:1) is the most preferred solvent used for the separation of lipids and especially animal fats. For vegetable oils, which are more polar than animal fats, Stahl et al recommended the use of petroleum hydrocarbon/diethyl ether/acetic acid (80:10:1 or 70:30:2).

Regarding the detection of lipids on TLC plates, Stahl et al indicated that neutral lipids are visualized by iodine vapors, 2',7'-dichlorofluorescein, or Rhodamine B. Both the iodine fuming and Rhodamine B reagents have a detectability limit as low as 1 μg, while 2',7'-dichlorofluorescein has a detectability range between 1 and 5 μg.

Both Stahl et al [12] and Kirchner [13] mentioned the use of reverse-phase chromatography as a means of TLC separation of lipids. Gurkin[4] stated that the use of reverse-phase silica gel plates may be beneficial because of the slight polarity evident in the lipid compounds. Specifically, he recommended a reverse-phase solvent system of acetonitrile/water (65:35).

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[4] Dr. Martin Gurkin, chemist, E. Merck Laboratories, New York, personal communication.

Separation Methods for Inorganic Ions

As prior contact with various lead manufacturers had determined that clays and graphites contain inorganic ion impurities together with their major elemental components, the use of TLC separation of inorganic ions was considered. It was determined that a number of research chemists had used various solvent systems on cellulose plates and had experienced varying degrees of success in the separation and identification of inorganic ions [14-18].

The primary disadvantage with these separation techniques was that every TLC separation method required that the metal ions exist in solution prior to their plate spotting. Any inorganic TLC analysis of the metal elements contained in the pencil clays required that the solvent system be capable of extracting these metal ions from their clay matrix. A review of the literature failed to identify any inorganic solvent system capable of effecting this separation.

Definitions of Lead Components

Waxes—The term "wax" is broadly applied to a variety of materials, both components and finished preparations. Historically, waxes are substances having characteristics somewhat like beeswax. Chemically, waxes are esters of fatty acids and monohydric fatty alcohols. Physically, waxes are water-repellent solids having useful degrees of plastic characteristics. Functionally, waxes provide filling, sealing, polishing, and candle-making properties.

Waxes are widely distributed in nature and found in the following classifications: animal (including insects), vegetable, and mineral. They are used in industry in a variety of applications including paper coating, polishes, electrical insulation, carbon paper, textiles, leathers, precision casting, and pharmaceuticals.

Solubility of waxes varies widely in different fat solvents and is dependent on temperature. Generally, complete solution is obtained at temperatures approaching the melting point of the wax and the boiling point of the solvent. Although wide variances exist between different wax products, common analytical tests include hardness, melting point, refraction index, specific gravity, moisture, suspended content, ash, unsaponification hydrocarbons, and resin content determinations and identification of acid, saponification, and acetate numbers [19]. The chemical definitions of several of the leading manufacturers' wax components are set forth below.

Carnauba wax is obtained from the leaves of the carnauba palm in the semiarid northeastern part of Brazil. It dissolves well in hot turpentine or naphtha and has good solvent retention power. The chemical properties include 85% alkyl esters of higher fatty acids. It is the hydroxylated saturated esters that give carnauba its extreme hardness.

Candelilla wax is obtained from a perennial weed growing in the semiarid regions of northern Mexico. It is a hard, brittle wax like carnauba and is the preferred vegetable wax in chewing gum formulations. It is brownish and melts at 66 to 78°C. Most vegetable waxes are esters of aliphatic acids, although candelilla contains 51 to 55% hydrocarbons and less than 30% esters.

Japan wax is the fat from the berries of a sumac-like tree cultivated in Japan and China for its wax product. It has a low melting point (55°C). It is primarily tripalmitin and has over 5% glycerol ester component. It is used in the textile industry as a finishing formulation and is actually a vegetable tallow, since it is composed of 90 to 91% glycerides.

Stearic acid has the chemical formula $CH_3(CH_2)_{16}(COOH)$. It is nature's most common fatty acid, derived from natural animal and vegetable fats, insoluble in water but soluble in alcohol, ether, and chloroform. It melts at 70°C and is used as a general lubricant [19].

Animal Waxes—Tallow wax is an animal fat with carbon chains containing 16 to 18 carbon atoms and is derived from cattle, sheep, and horses [20].

Clays—Clays originate as rocks (consolidated or unconsolidated) and are usually composed of one or more of the clay minerals (hydrous silicates of aluminum, iron, or magnesium) with or without other rock and mineral particles. They are characterized by fineness of particles, wide variations in physical and thermal (ceramic) properties, and differences in mineral and chemical compositions. The so-called primary clays are those found in their natural state while the secondary, or sedimentary, clays have been deposited after weathering (kaolin clays from Georgia).

Clays differ in their clay mineral components, the amount and type of non-clay material, the particle size distribution, particle shapes, and the amount and kind of exchangeable ions and soluble salts. The largest volume uses of clays are in the manufacture of ceramic products and as fillers in rubber goods, plastics, and paper products.

The study of crystalline clay minerals today includes the use of the polarizing microscope, chemical analysis, infrared absorption, and X-ray or electron powder diffraction patterns.

The mineralogy of clay mineral particles was poorly organized until the development of more sophisticated instrumental techniques (especially the X-ray spectrometer). The clay types used in the production of pencil leads are all of the crystalline variety and include (in both their combined and pure states) kaolin and montmorillonite. A U.S. Geological Survey Study [21] of these mineral groups was conducted and the results are incorporated in Tables 1 and 2.

Collection of Samples

The eight U.S. graphite lead manufacturers include Faber-Castell, Berol Corp., M. A. Ferst Ltd., Jensen Corp., Empire Pencil Co., Everhart-Faber Co., Dixon Crucible Co., and General Pencil Co. These manufacturers are responsible for providing the graphite lead cores to the 17 major pencil-manufacturing firms for the production of their finished pencils.[5]

Letters were sent to the lead manufacturers requesting them to provide samples of their major lead constituent products, including graphites, clays, and waxes in both pure and combined states.

TABLE 1—*Chemical analyses of the kaolin minerals.*

Component	Kaolin Clays						
	1	2	3	4	5	6	7
SiO_2, %	45.44	52.46	40.26	46.5	45.78	42.68	44.90
Al_2O_3, %	38.52	32.20	37.95	39.5	36.46	38.49	38.35
Fe_2O_3, %	0.80	1.69	0.30	...	0.28	1.55	0.43
FeO, %	...	...	...	...	1.08	...	...
MgO, %	0.08	none	...	...	0.04	0.08	trace
CaO, %	0.08	0.03	0.22	...	0.50	...	trace
K_2O, %	0.14	0.31	} 0.74	...	} 0.25	0.49	0.28
Na_2O, %	0.66	0.25		...		0.28	0.14
TiO_2, %	0.16	0.55	...	...	...	2.90	1.80
H_2O removed at 105°C, %	0.60	1.38	4.45	...	2.05	...	...
H_2O removed at higher temperature, %	13.60	12.07	15.94	14.0	13.40	14.07	14.20
Total	100.08	100.94	99.86	100.0	99.84	100.54	100.10

[5] Andrew Torok, Faber-Castell Corp., personal communications.

TABLE 2—*Chemical analyses of the montmorillonite minerals.*

Component	Montmorillonite					
	1	2	3	4	5	6
SiO, %	51.14	42.28	43.51	55.86	42.99	34.46
Al_2O_3, %	19.76	20.27	2.94	0.13	6.26	16.95
Fe_2O_3, %	0.83	8.68	28.62	0.03	1.83	6.21
FeO, %	...	...	0.99	...	2.57	...
MnO, %	trace	...	...	none	0.11	...
ZnO, %	0.10	...	...	...	...	23.10
MgO, %	3.22	0.70	0.05	25.03	22.96	1.11
CaO, %	1.62	2.75	2.22	trace	2.03	...
K_2O, %	0.11	trace	...	0.10	trace	0.49
Na_2O, %	0.04	0.97	...	2.68	1.04	...
Li_2O, %	...	...	...	1.05	...	...
TiO_2, %	none	...	...	none	...	0.24
F, %	...	...	...	5.96	...	...
H_2O removed at 150°C, %	14.81	19.72	14.05	9.90	13.65	6.72
H_2O removed at higher temperature, %	7.99		6.62	2.24	6.85	10.67
Total	99.75	100.37	100.02	102.98	100.29	99.95

Six of the eight lead manufacturers provided the requested samples of their product components. An inventory of the products received is described in Table 3. It should be noted that two of the firms (M. A. Ferst and Dixon Crucible) did not provide samples of their product components until after all analytical examinations (both chemical and instrumental) had been completed. Therefore, their samples are not included in this study.

Product Information

Several of the manufacturers provided information on the physical and chemical nature of their individual lead components. Most graphite pencils contain both amorphous and crystalline graphites. The amorphous is black and unctuous while the crystalline is shiny and scaly.[6] The most popular grades of writing leads are the #1, #2, #2½, #3, and #4. One manufacturer reported that 80% of his firm's pencils comprised the #2 and #2½ grades, while the #3 grade comprised about 15% with the remaining 5% accounted for by the #1 and #4 grades (Footnote 5). This same manufacturer provided the clay contents (±0.5%) of the firm's pencil leads as follows: Grade #1, 30%; Grade #2, 36%; Grade #2½, 43%; Grade #3, 50.5%; and Grade #4, 53%.

Relevant data pertaining to lead components was provided by a third manufacturer, and the following is a portion of his written response:[7]

All graphite writing cores are kiln-fired at 1000°C, which subjects them to chemical changes. Clay, a product of nature, requires constant monitoring during the manufacturing process. The variables are minor impurities of both organic and inorganic materials. Other variables are the age and depth of the strata at which the clay was mined. While the strata may be chemically identical, they do process differently. This would require minor adjustments in processing which really do not reflect a major formula change but are different. The firing does change the clay structure and no doubt its chemical composition due to the loss of water of crystallization, other volatiles, and finally to its new vitrified form. I do not know the final chemical identity. In

[6] Oscar Weissenborn, General Pencil Co., personal communication.
[7] Ted Kaye, Everhart-Faber Corp., personal communication.

addition, certain losses occur in the graphite phase, mainly coversion to other forms of carbon, and/or carbon monoxide and dioxide. The change is kept to a minimum by using a reducing atmosphere in the furnace and excluding as much air as possible by insulating the saggers. These controls produce a viable product from a consumer standpoint. However, from your viewpoint, and using your sophisticated analytical disciplines, these subtle changes will prove to be a nightmare.

These same subtle changes may, however, prove to be a blessing for forensic identification and dating purposes.

Methods for Lead Analysis

A few of the lead firms contributed suggestions for the analysis of their respective lead products. One firm suggested that, through microscopic examination of the written line, one could conceivably distinguish between the reflective qualities exhibited by a word written with a low percentage of crystalline lead (Footnote 6). Another firm recommended an analysis of the ignition residue (clay content and graphite ash) for identifying grade or manufacturer's product (Footnote 5).

Inasmuch as the forensic identification of pencilled writing would normally involve the in-situ analysis of the graphite lead as it exists in a line of pencil writing, it appeared necessary to determine the weight of pencil lead deposited per unit length of writing. One lead manufacturer determined through the use of company calibration and quality control testing equipment that the application of 200 grams-force of pressure with a #2 lead pencil on a 25% rag content paper will produce 0.0894 g of lead deposit (with variability error of ±0.005) along 25 m (1000 in.) of line (Footnote 5).

Results and Discussion

Physical (Nondestructive) Analysis

When matter is illuminated with light energy consisting of a broad band of wavelengths in the ultraviolet (UV) and visible spectrum, one of a combination of effects can occur:

1. Energy in some wavelengths is reflected.
2. Energy is absorbed by the substance.
3. Energy is absorbed at some wavelength and reemitted at usually longer wavelengths.

This last phenomenon is known generally as "luminescence" and refers to the principle that the wavelength of the emitted radiation is dependent on the chemical structure of the substance and usually not on the temperature.

It has been established that some of the components of inks are affected differently by infrared (IR) radiation illumination. Graphite, which appears in most ball-point inks, readily absorbs IR light, and the ink can be categorized by the amount of IR light reflected or absorbed [22].

It is known that inks will fluoresce with different intensities and colors under UV illumination. Ultraviolet fluorescence can be defined as short-duration luminescence caused by excitation with UV radiation and emission in the UV or visible spectrum.

Both IR luminescence and UV fluorescence are useful phenomena for the document examiner. Some of their applications include the differentiation of inks, paper, adhesives, or other materials used to prepare documents. The examination of the TLC chromatograms under UV or IR light may be beneficial in viewing and distinguishing between separated compounds.

Based on the successful application of IR and UV techniques in the analysis of both organic and inorganic substances, samples of the individual lead components (graphites, clays, and waxes) of different manufacturers were exposed to different wavelength illumi-

TABLE 3—*Inventory of product samples.*[a]

Firm	Waxes	Clays	Graphites	Pencils (Grades)
A	aluminum stearate, low and medium gel; double-pressed stearic acid; glycerine; Hyfac 531 and 2131; Neustrene 45	B.C.; hydrated special; pencil Clay B (concentrated); pencil clay modifier; Kentucky-Tennessee	508; 1845; 2095	1, 2, 2½, 3, 4, 860/2, resin-base
B	Toranil B; carnauba; Hercolyn D	Kentucky-Tennessee; kaolin; bentonite	amorphous, flake, semicrystalline	2 (3 different formulations)
C	Japan, oleic acid, candelilla wax	kaolin, montmorillonite, bentonite-montmorillonite combination	amorphous and semicrystalline (3 different formulations)	1, 2, 3, 3½, 4, 5, 6, HB, B, F, layout, Justrite, Ebony
D	refined glycerine wax combinations	B.C., Kentucky-Tennessee, kaolin, Schippach	5151, 986, 900, Siberian, Lonza synthetic	1, 2, 2½, 3, 4, (waxed and un-waxed)
E	Hercolyn D, tallow, B-3	Schippach	amorphous, semicrystalline mixed	1, 2, 2½, 3, 4, layout
F	mixed (type unknown)	Schippach		1, 1½, 2, 2½, 3, 4
G	mixed (type unknown)	2 different formulations (type unknown)	4 different kinds (type unknown)	1, 2, 2½, 3, 4
H	B-3, stearic acid	bentonite, Suprex	508, 5151, 986, 900	none (does not make pencils)

[a]Because of proprietary agreements with each manufacturer, none of the firms' specific product components can be identified.

nation. As these techniques were employed to detect the possible existence of any luminescent or fluorescent lead components, all grades of the finished lead product were also exposed to UV and IR radiation. Also examined was a sample of a Pentel pencil lead, which is a specific type of high-polymer lead based on a synthetic resin.

The results of all of the UV and IR tests proved negative as far as detecting any type of fluorescent/luminescent characteristics associated with any of the different lead specimens.

Microscopic Examination

Since it has been established that different lead manufacturers employ different graphite and clay products (in different proportions) in the production of their finished leads, microscopic examination of the components was conducted in an attempt to differentiate between various pencil leads. High-power microscopic examination ($\times$650) of seven different grades of Empire pencil lead disclosed a difference between the amorphous and crystalline graphite particles under regular light. Under polarized light, microscopic examination revealed differences between the graphite and clay particles, but it was not possible to characterize the different types of clays by examination of their physical characteristics.

It may be possible to differentiate among the various types of pencil leads through microscopic examination of their individual components, but further study is required.

Extraction Methods

Waxes—Almost all vegetable waxes are soluble in benzene [19]. In the case of carnauba wax, the use of benzene (both at room temperatures and heated) was unsuccessful in extracting the wax components for TLC purposes. Although heated naphtha and turpentine solvents have been recommended for carnauba wax, the maintenance of high temperatures is not practical for room-temperature TLC procedures because of the gelling effect observed on cooling (confirmed experimentally).

With the exception of carnauba wax (which is not used as a primary wax ingredient), all other waxes analyzed were successfully dissolved in benzene. Also, carbon tetrachloride has been recommended as a dissolving agent for carnauba, but tests conducted with this recommended organic solvent proved negative (Footnote 5).

Inorganics—Standard procedures for the chemical analysis of clays and clay-related products have been developed.[8] The analytical procedures include the recovery of silica (SiO_2), aluminum oxide (Al_2O_3), iron oxide (FeO_2), titanium oxide (TiO_2), alkaline earth oxides (CaO and MgO), alkalies (Na_2O and K_2O), and phosphorous pentoxide (P_2O_5) from the bulk clay sample. All of the procedures involved lengthy and fairly complicated fusion, filtration, ignition, colorimetric, and acid precipitation techniques and were initiated with bulk quantities of the various clay materials. As the amount of clay (by weight) evident in a #2-grade written pencil line will probably be in the microgram range (and certainly no more than 1 mg), the use of the chemical extraction procedures was considered impractical for sample sizes of forensic interest.

As attempts to identify an appropriate inorganic solvent system capable of extracting the metal ions from their clay matrix proved unsuccessful, it was concluded that some form of X-ray spectrometric analysis might be beneficial for trace element characterization.

Chemical Analysis of Waxes

Individual Components—Utilizing the solvent system recommended by Stahl et al [12] for the differentiation of plant and animal waxes on silica gel, we used a system consisting

[8] Vincent Sallese, Faber-Castel Corp., "Standard Method No. 1510—Chemical Analysis of Clays."

of a mixture of petroleum hydrocarbon/diethyl ether (95:5). The detection reagents included both 2′,7′-dichlorofluorescein, 0.1% (1- to 5-μg sensitivity range), and Rhodamine B, 0.25% (as little as 1-μg range sensitivity).

The first experiment involved applying equal volumes of the dissolved waxes obtained from General and Berol lead manufacturers onto a precoated silica gel Merck plate (without fluorescent indicator). It should be noted that all TLC separation experiments involved equal amounts of benzene (or other organic dissolving agent) being applied to each plate as a control to insure against contamination of results. The spotted plate was placed in a developing tank containing a suitable amount of the 95:5 solvent system for 20 min. The plate was allowed to dry and then sprayed with 2′,7′-dichlorofluorescein spray reagent. Visible inspection of the plate revealed that the waxes did fractionate at different R_f values and appeared as light yellow spots against a deeper yellow background. Under UV illumination, the characteristic spots fluoresced brightly and enhanced the ability to distinguish among the separated compounds. However, two of the three General waxes possessed relatively the same R_f values and proved difficult to differentiate.

Each of the dissolved Berol and General waxes was applied sequentially in multiple spottings to ascertain the effect of concentration differences on the developed spots. Again the silica gel plates were employed, as were the same solvent system (hereafter referred to as System 1) and reagent spray. The developed plates revealed adequate separation, although with increasing amount of concentration the spots appeared less distinct in form and tended to have a tailing effect.

Referring to previous information on reverse-phase TLC organic solvent systems (Footnote 4), we used an additional solvent system (Solvent R.P. 1) which consisted of a mixture of acetonitrile and water (65:35). Additional TLC chromatograms consisting of dissolved samples of the same previously tested four waxes in the R.P. 1 system and spotted on precoated silica gel 60 (reverse-phase) Merck plates were developed. The developed spots were again treated with 2′,7′-dichlorofluorescein spray reagent. The resultant plates failed to disclose any fractionation effect and no separation of the wax components was achieved.

A decision was made to change organic solvent systems in accordance with the procedures recommended by Stahl et al [12]. Consequently, the following additional systems were developed: System 2, petroleum hydrocarbon/diethyl ether/acetic acid (80:10:1), System 3, petroleum hydrocarbon/diethyl ether/acid (70:30:2); and System 4, petroleum hydrocarbon/diethyl ether/acetic acid (90:10:1). On three separate silica gel plates, spots of the same amounts of the previously examined waxes were developed in each of the three systems. The results clearly indicated that the best separation of components was achieved with System 2 and in all additional tests this system was employed in the development process, as was Rhodamine B 0.025% reagent (for more sensitive detection limits than 2′,7′-dichlorofluorescein).

Two separate tests were then conducted in an attempt to check the consistency of fractionation obtained under the same TLC operating conditions. System 2 was used in combination with Rhodamine B on the same type of precoated silica gel TLC plates. The developed plates showed consistent separation throughout all samples of the eleven different waxes tested. As stated earlier, no extraction of the carnauba wax was effected with the benzene agent.

Chromatograms of each firms' standard wax products were then produced for comparison. Standard chromatograms of the different uncombined waxes revealed different R_f values for all tested products.

Combined Products—Contact with representatives of Faber-Castell, Berol, Dixon Crucible, and Everhart-Faber disclosed that all of their pencil leads are treated with the same waxes or wax combination although different grades absorb varying quantities of the wax constituents. Several artificial mixtures of the waxes belonging to the same manufacturer

were produced and equal amounts of the combined substances were spotted on the same silica gel TLC plate. Development with System 2 and Rhodamine B disclosed that although there was adequate separation of some of the wax components to permit identification, there was some overlap because of the poor separation of a number of the other wax products.

Testing of the combined wax products supplied by two of the manufacturers disclosed that they consistently fractionated at different R_f values and hence were readily distinguishable.

Waxes from Pencils—The same measured amounts (100 $\pm$ 10 mg) of the five different grades of waxed lead cores supplied by Faber-Castell were exposed to equal amounts of benzene. After 15 min in solution the extracted components were spotted on a silica gel plate and allowed to develop for 30 min in System 2. After drying, the plate was sprayed with Rhodamine B. Inspection of the plate indicated that there had been successful fractionation of the wax constituents from the combined and finished lead samples. This result indicated that the same solvent system could be used in the TLC examination of all manufacturers' finished lead products.

Separate chromatograms developed under the same operating conditions (System 2 and Rhodamine B) were obtained from each of the contributing manufacturers' lead products in each of their primary grades. On occasion, the chromatograms of the lead products of a couple of different firms revealed that the extracted wax components found in the different grades had fractionated at different R_f values. This result indicates that some of the manufacturers alter the way components are combined in selected grades of lead and again aids in differentiating among grades. Comparison of all chromatograms disclosed that each manufacturer's lead organic component (wax) fractionated at a different R_f value, thus permitting a means of differentiating among manufacturers' leads by identification of characteristic dissimilarities appearing in the chromatograms.

An examination of the developed spots obtained through appropriate TLC analysis of eight different #2 pencil leads obtained from six different manufacturers disclosed the pertinent R_f values given in Table 4.

On some of the chromatograms the R_f values corresponding to the extracted wax products obtained from their respective finished lead hosts did not correspond exactly with the R_f values obtained from the TLC analysis of the uncombined waxes associated with that particular firm. This difference was explained by one firm representative as being attributable to the change in physical and structural characteristics which occurs to waxes on heating. The heating process tends to alter the chemical composition and thus can affect the absorbability on the silica gel plate, which results in changes in the R_f values in the finished form on pencil lead. Another observation was that the amount of wax extracted from equal weights of lead of increasing hardness varied among manufacturers. This is a reflection of the various mechanical methods of adding the waxes to the lead products. Some firms, for example, simply dip their unwaxed lead cores into a vat of

TABLE 4—*The R$_f$ values of eight #2 pencil leads.*

Pencil	Spot 1	Spot 2	Spot 3	Spot 4
A	0.175	0.650	1	0
B	0.425	1	0	0
C	0.300	0.650	1	0
D	0.600	1	0	0
E	0.300	0.600	0	0
F	0.250	0.550	0	0
G	0.175	0.550	1	0
H	0.225	0.525	0.800	1

heated waxes while other firms use a centrifuge-type device that impregnates the pencil lead core with the wax(es). For a variety of reasons, the wax is not always distributed uniformly along the lead core, causing variances in the wax concentrations. Still another explanation centers around the wax's specific gravity (or softness/hardness characteristics) as a critical factor in determining its ability to be dissolved. One firm advised that whereas their #1-grade pencil lead will usually absorb between 6 and 8% by weight of the waxes, their #2-grade pencil will absorb between 10 and 12% percent.[9] This fact provides another example of how different wax treatment techniques can alter composition ratios among grades and can cause batch-to-batch variations in constituent products.

Evaluation of Tholl's Experiments

In an attempt to ascertain whether Tholl's earlier inorganic TLC experiments [1,7] on pencil leads had actually separated the inorganic metal ions from the finished lead samples, a modification of his work was conducted. Approximately 11 mg of the #2 leads obtained from Berol, General, Faber-Castell, and Everhart-Faber were placed in vials in which 2 or 3 drops of benzene had been added to extract the wax components. After 1 h the treated unwaxed lead samples were placed in separate vials to which a drop of 10% nitric acid was added. Equal amounts of the resultant lead components were spotted on both silica gel and cellulose plates together with spottings of the extraction solvent which acted as a control. The plates were developed in Tholl's recommended solvent system [7] consisting of n-butanol/glacial acetic acid/distilled water (80:20:20). Following development, the dried plates were sprayed with Kojic acid (0.1 g of acid dissolved in 100 ml of absolute ethanol), which reportedly detects metal ions [7]. The resultant cellulose TLC plate did not reveal any significant evidence of fractionation of the lead components.

At this point, it was suspected that Tholl's TLC experiments had failed to extract the inorganic metal ions from the lead and that his system had merely extracted the lead wax components. This conclusion is reasonable when one considers Tholl's use of carbon tetrachloride as a wax solvent, which allowed the extracted wax components to be spotted together with the lead product on the cellulose plate where it was subsequently fractionated.

This conclusion was confirmed by using Tholl's technique in the analysis of six different waxes that had been treated with carbon tetrachloride and 10% solution of nitric and hydrochloric acids. After being sprayed with Kojic acid, the developed plate revealed a chromatogram separation pattern similar to the plate obtained by Tholl.

Chemical Analysis of Inorganic Ions

Extraction from Solution—There is no satisfactory inorganic TLC system capable of extracting the trace metal ions from their clay matrix. Additional experiments were conducted with Tholl's recommended n-butanol system [7] on the individual clay products.

Equal amounts of 14 different clays (excluding those of Dixon Crucible and M. A. Ferst) were treated with two drops of a 10% nitric acid solution and then spotted on a cellulose plate. A second cellulose plate was treated in the same manner except that a 10% hydrochloric acid solution was applied to the clays and a third cellulose plate included a 10% solution of both hydrochloric and nitric acids. Investigating the possibility that enhanced extraction of clay components could be accomplished with a more concentrated acid solution, we prepared a fourth cellulose plate under the same TLC operating conditions, using a 10% concentrated mixture of hydrochloric and nitric acids. Following development in the n-butanol system, the most effective separation was achieved with a test using a 100% concentrated acid solution.

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[9]Dr. Wallach, chemist, Empire Pencil Co., personal communications.

In an attempt to ascertain whether the characteristic band of pyramid-shaped spots observed at approximately the same R_f value were truly metal ions extracted from the individual clay products, a separate comparative TLC experiment was conducted. This test involved the selection of four different clays (following acid treatment) and samples of titanium, magnesium, silicon, calcium, aluminum, and iron (major metal ingredients of clay), each of which was treated with a solution of 100% hydrochloric acid and 100% nitric acid before being spotted on a cellulose TLC plate. The plate was developed in the *n*-butanol system and sprayed with Kojic acid. The chromatogram showed a somewhat similar pattern of fractionation between that obtained from the clay and that achieved from the iron oxide (FeO).

This experiment suggested the possibility that inorganic TLC methods utilizing the *n*-butanol system may successfully separate the iron ions from both the clay and lead but has limited value in the extraction of any other metal elements.

Instrumental—X-ray fluorescence spectrometric analysis is a nondestructive instrumental method of qualitative chemical analysis for elements based on measurement of the wavelengths and intensities of their X-ray spectral lines emitted by secondary radiation [23]. The X-ray fluorescent spectrometer used in this study's analysis of inorganic trace metal elements contained within pencil lead was a Diano XRD 7, a wavelength-dispersive-type instrument. This device causes the spectral lines of all elements to be simultaneously excited and then separated on the basis of their wavelengths by an analyzer crystal. The function of the crystal is to disperse the X-ray beam from the specimen, causing each spectral line to deflect into a different direction. Different crystals are required for different wavelength regions, and in this test pentaerythritol (PET) and "thalium acid pthalate" (TAP) crystals were employed in the X-ray analysis of the lead samples. The detector converts each incident absorbed X-ray photon into a pulse of electrical energy having an amplitude proportional to the incident photon energy. Both gas proportional and scintillation counters were employed as detector devices in these experiments.

The target material in the X-ray tube was chrome and therefore the chrome peaks developed in the sample spectra were ignored in the evaluation of elemental composition.

Some manufacturers combine different clay products in differing proportions into their finished lead cores. As all types of clay differ in their own mineral components and in the amounts and kinds of exchangeable ions, these characteristic elemental differences should be detectable through X-ray fluorescent techniques.

The experiments involved the preparation of each lead sample by first weighing approximately the same amounts (103 ± 3 mg) for each of the #2 grades of lead furnished by six different manufacturers. These samples had first been pulverized and had passed through a 180-μm (#80) sieve for size uniformity. Equal amounts of cellulose (approximately 400 mg) were added to each sample to create a suitable noncontaminating backing material for the lead. These lead samples were then formed under extensive pressure (103 MPa or 15 000 psi) into disks and then exposed to X-rays for analysis.

Specific X-ray spectra were obtained from each of the manufacturer's lead products after exposure to both PET and TAP crystals. The qualitative differences among spectra were determined by the appearance of specific peaks at characteristic wavelengths associated with the clay mineral elements. Quantitative differences were determined by measuring peak height ratios obtained for certain elements. Only the major mineral constituents were analyzed for comparative purposes, including iron, titanium, aluminum, calcium, potassium, silicon, magnesium, and phosphorus. The minor trace elemental differences were ignored in the overall evaluation process (Figs. 1 to 4).

The peak height ratios for the same elements often differed among manufacturers and provided another means of differentiating between the clay metal components. The most valuable differences in elemental ratios included the calcium/iron and potassium/iron figures. Because of the confidential and proprietary nature of much of the information
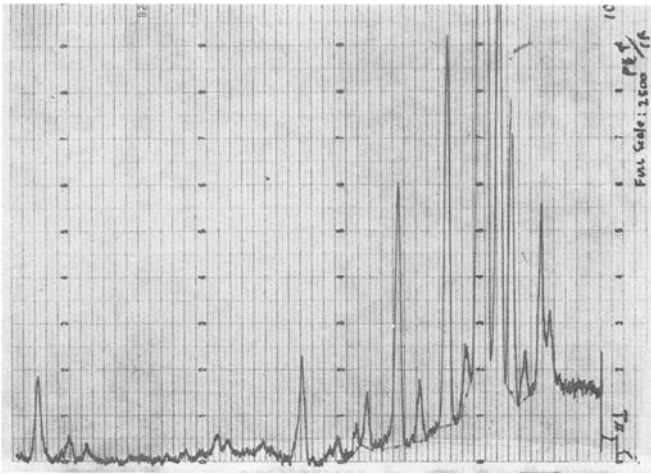
FIG. 1—*Photograph of X-ray spectra obtained from analysis of lead sample provided by Company A (PET crystal).*
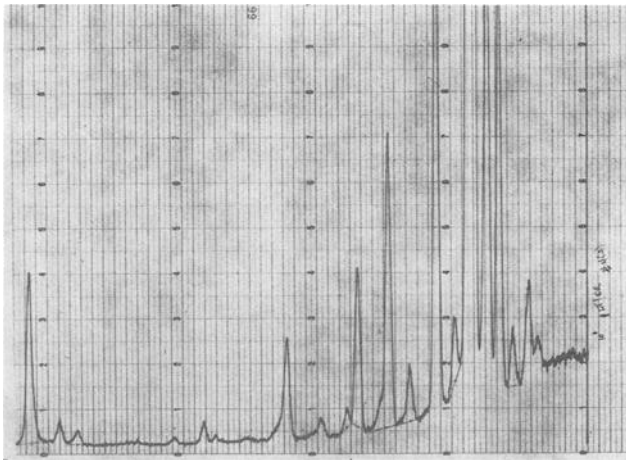

FIG. 2—*Photograph of X-ray spectra obtained from analysis of lead sample provided by Company B (PET crystal).*

provided by the manufacturers relative to their product composition, the specific quantitative values obtained from these X-ray tests will not be reported in this study.

Pencil Writing on Paper

An effort was made to develop a TLC technique of analyzing pencil lead writing extracted from paper. The extraction technique was the same developed earlier by ATF chemists in the analysis of writing inks [24] and involved the use of a scalpel which, when properly employed, could remove an actual line of pencil writing from a piece of paper. In this part of the study, three separate TLC experiments were conducted.

The first involved the scalpel recovery of 254 mm (10 in.) of pencil writing from What-
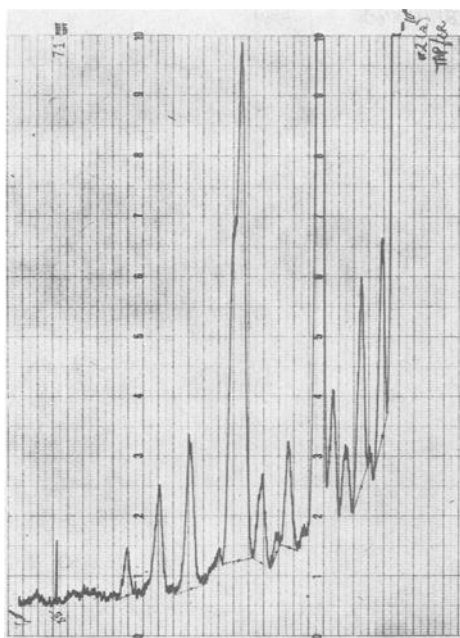
FIG. 3—*Photograph of X-ray spectra obtained from analysis of lead sample provided by Company A (TAP crystal).*
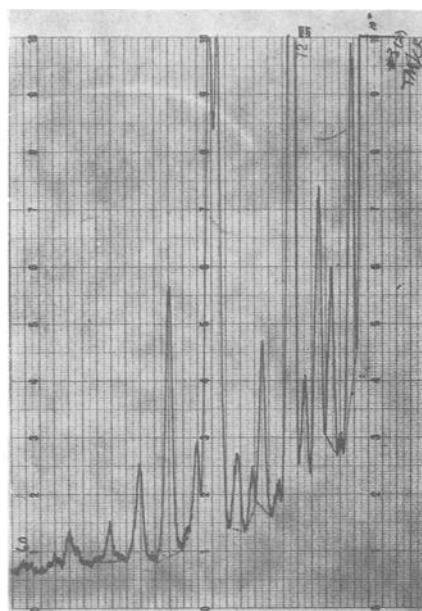
FIG. 4—*Photograph of X-ray spectra obtained from analysis of lead sample provided by Company B (TAP crystal).*

man paper (high rag content paper with few artificial fillers or coatings) of Empire #2 lead. The 254 mm (10 in.) of pencil writing should have produced a sufficient amount of lead deposit for TLC analysis purposes based on Torok's reported results obtained from his firm's calibration equipment (Footnote 5). A strip of paper containing no lead deposit was used as a control. Seventeen drops of benzene were applied to the Kontes® vials containing the combined lead and paper fibers, and, after a suitable interval, equal amounts of the sample and control specimens were spotted on a silica gel TLC plate. Solvent System 2 was used in the plate development, as was Rhodamine B reagent spray. No appreciable fractionation of constituent products was observed.

In two additional tests, 508 and 762 mm (20 and 30 in.) of pencil writing were extracted and analyzed under the same TLC conditions. The first test involved the use of twelve different #2 leads supplied by six different manufacturers while the second test involved the examination of three different #2 lead samples. A paper control was used in both of these tests. Although the developed plates did reveal faint but consistent spots of the same R_f value for each of the tested lead samples, this same characteristic spot phenomenon was repeated in both instances in the paper control.

These results indicated that there must be some interfering agent or agents in the paper that preclude the extraction of the wax components from their respective lead hosts.

Conclusion and Summary

Efforts were made to distinguish pencil leads both chemically and instrumentally and to determine the feasibility of identifying a manufacturer's product as having been used in the execution of a questioned pencilled writing. By application of the proper TLC operating

conditions, a successful differentiation among lead manufacturers' products is both possible and practical. These operating conditions include the use of Merck precoated silica gel plates; benzene as the wax solvent; the proper solvent system (petroleum hydrocarbon/diethyl ether/acetic acid (80:10:1); Rhodamine B reagent; and UV illumination and photography. The sensitivity limits of this procedure allow detectability and separation of the wax components as low as 1 mg of sample weight.

A successful instrumental technique for differentiating among the elemental compositions imparted by the clay constitutent in the combined lead products of different manufacturers was developed with the use of appropriate X-ray fluorescent spectrometry techniques. Comparisons of selective elemental ratios of various clay metals permit identification among the different lead products.

Attempts to extract sufficient lead wax components from lead deposits on paper to permit identification of manufacturer's product through organic TLC procedures proved unsuccessful. The contaminating effects caused by the various paper agents will seriously interfere with any TLC attempt to identify lead products.

Organic TLC appears not to be a sensitive enough procedure for analysis of wax components removed from a written pencilled line. Possible future alternatives for the extraction and analysis of the organic lead constituents include liquid chromatography, gas-liquid chromatography, micro-IR (diamond cell), and microscopy techniques.

The identification and comparison of the inorganic components in pencil lead can be accomplished through trace elemental analysis such as X-ray fluorescence spectrometry. No attempt was made to detect trace metals from lead deposits on paper; however, the encouraging results obtained from lead analysis (in bulk forms) and the known sensitivity limits of certain instrumental techniques suggest that such procedures should prove promising. These inorganic analytical techniques would include the X-ray milliprobe, scanning electron microscope, ion microprobe, electron microprobe, and X-ray diffraction.

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