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# SPECTROGRAPHIC ANALYSIS AS AN AID IN IDENTIFICATION PROBLEMS

CHARLES M. WILSON†

Spectrographic methods of analysis and comparison are gaining rapid recognition and application in industrial and research laboratories. Unfortunately, however, spectroscopy has not found as wide use in the analytical identification problems submitted to the police laboratory as is warranted by its intrinsic value in many types of examination.

## CRIMINAL CASE

The following is the account of an actual case<sup>1</sup> which involved the use of the spectrograph, the only available means of analysis, comparison, and identification of the evidence in question, and it illustrates a technique which could be used to advantage in many cases of parallel nature:

During the early morning hours in a large eastern city, a police officer on duty in a squad car heard what he thought to be the sound of breaking glass. Going in the direction of the sound, the officer found a lone man upon an otherwise deserted street. The officer questioned this individual as to his identity and the reason for his being abroad at that hour of the morning. The suspect was unable to give a satisfactory explanation of his being in the neighborhood and was taken to the precinct station for further questioning and investigation.

On returning to the building in front of which the suspect had been apprehended, the officer discovered that a window had been broken in an outward direction, the glass having fallen in the street. An inspection of the interior further revealed that an entry had been effected from the rear, and that an unsuccessful attempt to burglarize a safe had been made.

A technical charge of vagrancy was placed against the suspected individual, and he was further questioned at the police station, but he only became evasive, and denied all knowledge of the attempted

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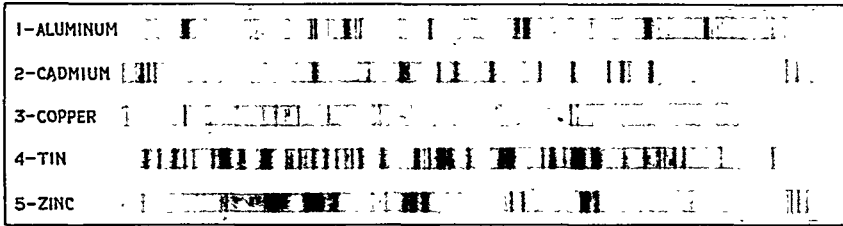
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<sup>1</sup>Submitted by Research Officer George Keenan, Rochester Police Department, a former student of Crime Detection Methods at the Scientific Crime Detection Laboratory.



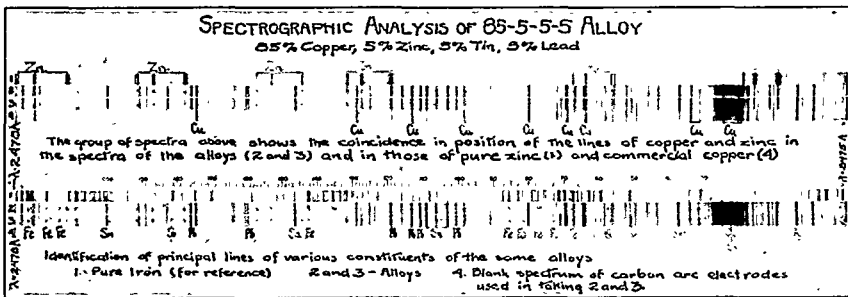
Courtesy of Bausch & Lomb Optical Co., Rochester, N. Y.

FIGURE 1—A, B, C, D.



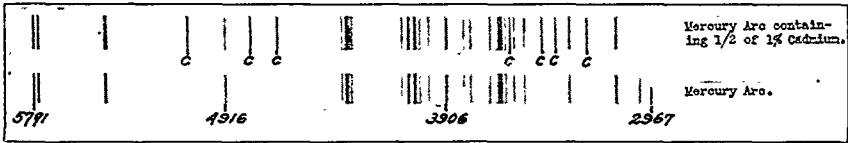
Courtesy of Bausch & Lomb Optical Co., Rochester, N. Y.

FIGURE 2.



Courtesy of Bausch & Lomb Optical Co., Rochester, N. Y.

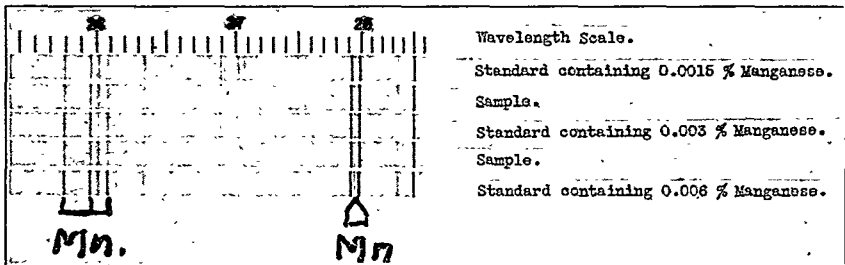
FIGURE 3.



Courtesy of Central Scientific Co., Chicago, Ill.

Lines designated by "C" are Cadmium Lines.

FIGURE 4.



Courtesy of Bausch & Lomb Optical Co., Rochester, N. Y.

FIGURE 5.

Manganese lines in sample spectrum are slightly stronger than those in the 0.0015% standard, and considerably weaker than those in the 0.003% standard. Manganese in sample estimated at 0.0018%.

burglary. The arresting officer noted a small stain or smear of red material on the blue wool jacket worn by the prisoner at the time he had been placed under arrest. The jacket was taken to a laboratory for examination.

The area of cloth containing the smear was carefully removed by means of a new razor blade and the red material removed from the fabric and given a preliminary microscopic examination, which showed it to be very similar in its general appearance to a sample of red putty taken from the broken window in the building in front of which the prisoner was found. The quantity of material from the garment of the suspect being insufficient for ordinary chemical analysis, a spectrographic analysis was chosen as the best means of analysis and comparison.

The exposures in juxtaposition (Fig. 1-A, B, C, D) were made at the laboratories of a large optical company. Figure 1-A is an exposure of the regular iron arc for purposes of calibration and standardization. Figure 1-B is an exposure using putty from known source other than the burglarized premises; Figure 1-C, the sample from the garment of the suspect; and Figure 1-D, the sample taken from the window through which the suspect was alleged to have made his escape or exit from the building. The similarity of spectral line distribution is at once apparent upon examination of Figures 1-C and 1-D.

There will be noted in Figures 1-C and 1-D certain dissimilarities in line spectra recorded. This probably is due to the presence of fibers and foreign material, transferred to sample from garment (probably fibrous material containing dyes), which did not exist in the sample used to make exposure 1-D. The preponderance of coincident lines, however, indicated both samples 1-C and 1-D were in all probability of the same material and from the same source.

Photographic enlargements of the plate were made, and presented to the grand jury. More than passing interest was shown in this type of evidence, and the prisoner was indicted promptly and when confronted with the evidence, he confessed and pleaded guilty without standing trial, receiving a suspended sentence of five years.<sup>2</sup>

#### TECHNICAL AND THEORETICAL ASPECTS

The value of spectroscopy in the field of forensic medicine has long been known.<sup>3</sup> Its use until comparatively recent years, how-

<sup>2</sup>State v. Kennedy (N. Y. 1933).

<sup>3</sup>Hoppe, "Characteristic Blood Spectra" (1862); Woodman and Weymott,

ever, has been restricted to problems of qualitative analysis of blood and vital organs of deceased persons to determine whether toxic or therapeutic quantities of substances were present at the time of death.<sup>4</sup>

The sensitivity or delicacy of spectrographic analysis in many instances exceeds that of ordinary methods of chemical analysis. For this reason, quantitative or qualitative spectrographic analyses must be conducted under the most rigorously controlled conditions. It is always essential to establish a control before comparison exposures are made.

In spectroscopy the instruments used to determine the emission or absorption characteristics of a substance generally fall in two classes, the spectrometer and the spectrograph. In a police laboratory the spectrograph undoubtedly will be preferred, since it permits the making of a photographic record which not only is the basis of conclusions reached but can be preserved indefinitely; if necessary, enlarged prints may be made for presentation in court.

Spectrometers or spectrographs are optical instruments which, by one of two methods, diffraction or refraction, break up the radiation entering the instrument into the component bands or wave lengths, and project them either upon an eye piece for visual inspection, as in the spectrometer, or, in the case of a spectrograph, upon a photographic plate or film so that a permanent record is made of the characteristic line or absorption spectra.

Within the last few years refinements and improvements have been made in the instruments and photographic emulsions<sup>5</sup> available,

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Forensic Medicine and Toxicology 509; Stokes, "Characteristic Blood Spectra" (1864).

<sup>4</sup>Hartridge, "The Coincidence Method for the Wavelength Measurement of Absorption Bands," Proc. Roy. Soc. 575-87 (1923); Autenrieth and Warren, Laboratory Manual for Detection of Poisons and Powerful Drugs 70, 305, 327, 663 (1928); Chamot and Mason, Handbook of Chemical Microscopy 283 (1931); Matthews, Physiological Chemistry 509, 1060 (1925); Witthaus and Becker, Medical Juris. Forensic Medicine and Toxicology 854, 865 (1929); Baly, Spectroscopy (1927); Robertson, Manual of Medical Jurisprudence and Toxicology 148 (1925); Webster, Legal Medicine and Toxicology 171, 174, 566 (1930); Smith and Glaister, Recent Advances in Forensic Medicine 160, 167 (1931); Lucas, Forensic Chemistry 41, 43, 282, 290 (1931); Pacini, "Ultra-Violet Detection of Mercury," I Am. Jour. Police Sci. 387 (1930); Adam Hilger, Ltd., The Detection and Investigation of Poisons by Spectroscopy; Nitchie, "The Application of Spectroscopic Apparatus to Industry," paper pres. A. S. M. E. (1930).

<sup>5</sup>Mees, "The Color Sensitivity of Photographic Materials," Jour. Franklin Inst. (1926); Eastman Kodak, Photographic Plates for Use in Spectroscopy and Astronomy (1933); *Ibid.*, Plates and Filters for Infra-Red Photography (1933); Baly, Spectroscopy (1927); Adam Hilger Ltd., The New Hilger-Schumann Plates (1931); Bur. Stds. Research Papers No. 488, 473. Scientific Papers Nos. 312, 372, 411.

so that the invisible portions of the spectrum (infra red,<sup>6</sup> ultra-violet,<sup>7</sup> and X-ray<sup>8</sup>) have been investigated, and the spectrographic determinations of these regions have added materially to the field of quantitative and qualitative analysis by this means.

The exploration of the extreme ultra-violet and X-ray regions by Saunders, Merton, McLennan, Millikan, and others have contributed much to the explanation of the nature of structure matter. Recent work in this field<sup>9</sup> (X-ray regions) indicates that refinements of techniques may prove to be invaluable in the identification of hairs and fibers.

All types of spectra may be said to fall in two distinct classifications—absorption and emission spectra. In the former a source of light having continuous spectral distribution is passed through the substance being examined, thence through spectrometer or spectrograph. This technique enables us to determine the particular regions which absorb or transmit the exciting source of illumination. In the second instance, that of emission spectra, the substance under examination is vaporized by one of the following methods: (1) Flame; (2) Electric arc; (3) Electric spark; (4) Electrically exploding fine wire; (5) Ionization of gas at low pressure by passage of electric current.

The value of emission or line spectra in analytical problems is dependent upon the fact that when the temperature of a gas is raised sufficiently it emits light or radiation of definite wave lengths which alone are dependent upon the molecular structure of the gases present and the method of excitation. This effect first was noted by Kirchoff and Bunsen.<sup>10</sup> (The spark line spectra characteristics of many elements are different from the arc spectra of the same element.)<sup>11</sup>

These groups of lines are known to exist only when the element producing them is present (Fig. 2). It may be in combination with other elements or it may exist alone (Fig. 3), but where a certain line or group of lines is observed which are characteristic of a certain

<sup>6</sup>Infra-Red discovered by F. W. Herschell (1800).

<sup>7</sup>Ultra-Violet discovered by J. W. Ritter, *Nicholson's Jour.* 214 (1804); Erickson and Edlen, "Spectra of The Light Elements in the Extreme Ultra-Violet," *Z. Physik*, 59, 656 (1930).

<sup>8</sup>Millikan, *Astrophys Jour.*, 52 (1920); 47, 53, 150 (1921).

<sup>9</sup>Astbury, "Adam Hilger X-Ray Fibre Spectrograph," publication, Adam Hilger Ltd. (1934).

<sup>10</sup>Pogg. Ann., 110, 160 (1860); 113, 337 (1861).

<sup>11</sup>Twayman and Smith, *Wavelength Tables for Spectrum Analysis* (1931); *International Critical Tables*, Vol. V (1929); *Bur. Stds. Sci. Paper No. 478*, "Redetermination of Secondary Standards of Wavelength from the New International Iron Arc.

element, the presence of that element has then been definitely established (Fig. 4).

Prior to 1913 a considerable amount of material had been collected on the behavior of line-spectra under various conditions of excitation. But there was no satisfactory explanation for the existence of line-spectra until Bohr's classical contributions which explained the existence of characteristic lines in terms of the atomic structure of matter and the quantum theory applied to monochromatic radiation. He was able by the use of a mathematical series to relate and explain the existence of line-spectra.<sup>12</sup>

The position of a line in the spectrum is indicated by the wave length ( $\lambda$ ) of the vibration which produces it. The unit of wave length is that Ångstrom unit. One Ångstrom is equal to  $10^{-10}$  meter. It is equivalent to  $10^{-8}$  cm. or  $.0001\mu$  where  $\mu$  is the micron or millionth of a meter. The limits of the visible portion of the spectrum extend from approximately 3900 Å on the violet to 7500 Å in the red. Obviously the use of the spectrometer is limited to this range, whereas the spectrograph may be employed not only to register radiation in the visible portion of the spectrum, but in the infra-red and ultra-violet portions as well.

The application of line-spectra, unfortunately, is limited almost entirely to inorganic qualitative and quantitative analytical problems, owing to the fact that the substance must be vaporized in order to excite it to a point where secondary radiation is produced. This involves raising the temperature to a point which will, in most instances, decompose organic substances.

#### GENERAL APPLICATION TO CRIMINAL INVESTIGATIONS

The type of criminological problem to which spectroscopy adapts itself is the qualitative or quantitative analysis of small amounts of substances, found either at the scene of a crime or on or associated with a suspected individual (e. g., putty as in the case previously discussed), which may furnish circumstantial evidence leading to the identification of the perpetrator of a given crime.

In certain types of problems the spectroscopic method has a decided advantage over chemical analysis. A much smaller quantity of a substance or material is necessary for spectroscopic analysis than for chemical analysis. Moreover, and possibly far more important, the spectrograph offers to a jury concrete evidence, in the nature of a photograph, of the results thus obtained.

<sup>12</sup>Johnson, Spectra 6, 11 (1928).



Every medico-legal laboratory should have available a spectrograph capable of rendering sharp line spectra images. Either the quartz or diffraction grating spectrograph is to be preferred, because many of the characteristic lines of the elements fall in the invisible portion of the spectrum (ultra-violet or infra-red regions). Such an instrument will lend itself admirably to rapid examinations of exhibits submitted for analysis.

Spectrographic methods of analysis applied in the types of examinations listed below may in many instances result in corroborative findings, as outlined in the case discussed in this article:

*Document Examinations: Inks, Erasures—*

In document examination, differences between inks, whether in liquid or the dry state, may be easily and rapidly determined. Also, documents which have been treated with some of the commercial two-stage eradicators for the purpose of removing ink inscriptions may be identified as such by spectrographic analysis.<sup>13</sup> Lucas<sup>14</sup> does not recommend these methods for general use for the reason that part of the document must be mutilated. This, in certain cases, is permissible, and spectrographic analysis would, under these circumstances, be recommended.

*Dust Traces—*

As an adjunct to the methods outlined in the excellent article by Locard,<sup>15</sup> spectrographic analysis would in many applications, yield results unobtainable by any other technique.

*Bullets—*

Traces of metal deposited upon fabrics by passage of a bullet may be detected spectroscopically by calcining fabric in an electric furnace and treating residue with nitric acid.<sup>16</sup> The composition of bullets may be determined accurately and is often of value in firearms identification problems.<sup>17</sup>

<sup>13</sup>Smith and Glaister, *Recent Advances in Forensic Medicine* 178 (1931).

<sup>14</sup>Lucas, *Forensic Chemistry* 98 (1931).

<sup>15</sup>Locard, "The Analysis of Dust Traces," *I Am. Jour. Police Sci.* 276, 401, 496 (1930).

<sup>16</sup>Amy and Boyle, "Sur un perfectionnement Aporté à la Technique de la analyse Spectrale," *Annals de Médecine Légale* 525-531 (1928).

<sup>17</sup>Smith and Glaister, *Recent Advances in Forensic Medicine* 178 (1931); Smith, "Spectrographic Assay of Some Alloys of Lead," *Inst. of Metals J.* 46,

*Paints, Varnishes, Lacquers and Resins—*

Very minute quantities of these substances may be examined spectroscopically after treating with nitric acid and calcining for the purpose of isolating and identifying impurities which occur in both standard and unknown.<sup>18</sup>

*Textiles and Fabrics—*

Characteristics of dye materials and metallic weighting of fabrics may be determined, and fabrics compared as to whether they are similar in chemical composition<sup>19</sup> (See Fig. 5).

*Bombs and Metallic Fragments—*

Supplementing metallurgical identification of bombs and fragments, spectrographic analysis in the type of investigation recorded by Mathews<sup>20</sup> would add corroborative proof of conclusions.

*Glass—*

Glass fragments lend themselves to identification by spectrographic analysis in much the same way as the evidence in the case recorded in this article.

*Precious Stones—*

Corroborative proof of the existence of artificial rubies.<sup>21</sup>

*Tools and Implements—*

Where improvised jimmies, black-jacks, brass knuckles, or tools are submitted for examination, the composition

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114-128; Twayman and Hitchen, Estimation of Metals in Solution by Spark Spectrum, Proc. Roy. Soc. 72-92 (1931); Baly, Spectroscopy (1927); "Quantitative Determination of Antimony, Tin and Cadmium in Lead Cable Sheaths by Means of Quartz Spectrograph," Brit. P. O. Eng. Dept. Res. Report No. 5651; Guenther, "Quantitative Spectrum Analysis of Lead Alloys," Zeits. Anorg. Allg. Chem. 409-418 (1931).

<sup>18</sup>Smith and Glaister, Recent Advances in Forensic Medicine 178; Iwamura, "Quantitative Spectrum Analysis," Kyto College Memoirs "A", 14, 43 (1931); *Ibid.*, 14, 327 (1931).

<sup>19</sup>Lewis, "Spectroscopic Analysis Ash Textiles," Textile Mfg. 338 (1930); Lewis, "Spectroscopic Investigation of Mineral Constituents of Textiles," British Woolen and Worsted Assn. Bulletin, 7-10 (May, 1930).

<sup>20</sup>Mathews, "Metallographic Analysis in Crime Detection," I Am. Jour. Police Sci. 439-443 (1930).

<sup>21</sup>Papish and O'Leary, Ind. and Eng. Chem. 11-13 (Analytical Ed., 1931).

can be analyzed and may lead to a source of the material from which the implement was fashioned.<sup>22</sup>

With the exception of post-mortem applications, the fact that literature in the field of spectroscopy contains very few accounts of the practical applications, or of the potential possibilities, of this method of analysis as applied to criminological problems suggests not the futility of such method of analysis but rather that this field represents practically virgin territory in the matter of research and adjudication.

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<sup>22</sup>Nitchie, "Some Practical Applications of the Spectrograph," *Ind. and Eng. Chem.* (1929); Baly, *Spectroscopy* (1927); Meggers, Kies and Stimson, *Bur. of Standards Sci. Paper No. 444* (1922); Nitchie and Standen, "An Improved Method of Quantitative Spectrographic Analysis," *Ind. and Eng. Chem.* 182 (1932); *Bulletin of Spectrum Analysis* No. 2, p. 2 (1930), No. 3, p. 6 (1931), Adam Hilger Ltd., London.