AN APPLICATION OF GEIGER COUNTER TUBES FOR SPECTROCHEMICAL ANALYSIS

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It has long been known that Geiger counter tubes, using the photoemissive effect of the cathode metal, can be applied to the measurement of very feeble visible or ultraviolet radiation. As a direct indicating instrument for measuring radiation intensities, the counter tube could be expected to offer special advantages in the detection of traces of chemical elements by their characteristic spectral emission lines. A simple apparatus based on this principle was designed and for several years successfully utilized for the detection of lead in the atmosphere of industrial areas.

The detection of traces of an element by means of its characteristic spectral lines emitted in an electric arc or spark is rather old. Kirchhoff and Bunsen used this principle first in the isolation and discovery of caesium and rubidium; Gerlach established the so-called "internal standard method" which enabled the principle to be used for precise quantitative analyses. In the last decade many industrial applications have been made, for example in the routine analysis of iron and steel for calcium, silicon, manganese, chromium, magnesium, and other elements. With modern equipment, the method is capable of high speed and precision 1).

The application of spectrochemical analysis which will be described in this article concerns the detection of lead in air. Atmospheric contamination by lead may occur in several branches of the chemical industry, due to small leaks in plant installations. Because of the well known toxic effect of lead, a maximum permissible lead concentration in air has been established in several countries. To make sure that the lead concentration in a plant does not exceed the limit of safety, a rapid means of analyzing air samples for lead is desirable.

When the problem presented itself in one of the E. I. du Pont de Nemours plants, spectrochemical analysis, because of its specificity and sensitivity, was considered to offer the best prospects for meeting the rather exacting requirements. A photographic technique was developed for the purpose 2).

In the plant where the purity of the air was to be examined, an electric spark was run continuously between two copper electrodes. The spectrum of the spark was photographed with the aid of a small quartz spectrograph. Part of the spectrum, consisting principally of copper lines, with a certain number of other lines attributable among other things to the water vapor content of the air, is shown in fig. 1a. If the air contains traces of a lead compound this is decomposed in the hot spark, and lead lines will appear in the spectrum. The most sensitive line, i.e. the line which appears at the lowest lead concentration, is the line at about 2203 Å, i.e. well up in the ultraviolet. A photograph of the copper spark spectrum with this lead line is shown in fig. 1b. Inspection of the photographic plate for the presence of this line enabled a lead concentration as low as one part in 50 million (on a weight basis) to be detected. This is about 7 times lower than the maximum permissible concentration of 0.15 mg lead/m³ air. The exposure time required

*) Philips Laboratories, Inc., Irvington on Hudson, N.Y., U.S.A.
1) Cf. for example R. Sawyer, Experimental Spectroscopy, Prentice Hall, New York 1944.
was about one minute. An approximate quantitative analysis was possible by comparing visually the intensity of the lead line with that of adjacent copper lines. Calibration was accomplished by comparison with chemical analyses performed on samples taken simultaneously from a common air stream.

Although the photographic method worked quite satisfactorily and the superiority of spectrochemical analysis over previously used chemical methods was striking enough, still its application was hampered by the fact that the method was essentially discontinuous. In the operation of a plant, safety measures should be based, not on the detection of too high a lead concentration in one place, but rather on the early discovery of an increase in the lead concentration as a function of time, revealing the presence of a leak in plant installations before dangerously high lead concentrations in the atmosphere are attained. Detecting such a trend of the lead concentration to increase and locating the leak by the photographic method lines which is given by the spectrograph can be dismissed (except for alignment and calibration purposes). The important advantage of the Geiger counter tube, provided with means for directly measuring the rate of arrival of the radiation quanta, lies in its being a continuously working, direct reading device. Such a device can serve the purpose of leak detection much better than any discontinuous method, as it will immediately reveal the trend of variation in the lead concentration. Thus, if the air to be analyzed is pumped to the spark gap by means of a long flexible hose with which the operator can scan pipes, valves etc. of an installation, a very effective method of leak hunting is obtained.

For reasons to be explained later, the Geiger counter method in the present case is not capable of a similar sensitivity and accuracy as the photographic method. However, for the restricted objective of locating areas of high lead concentration at possible leaks in plant installations, performance requirements are less severe and the Geiger counter method fully proved its ability to comply with them.

![Fig. 2. Apparatus for the detection of lead. The spark A between copper electrodes, condensed by a capacitor C, excites the lead contained in the air pumped through the spark housing by the blower B. The radiation emitted by the spark is dispersed by the spectrograph S; the adjustable exit slit T isolates the lead line 2203 Å, which is measured by the Geiger counter tube G. H is the high voltage supply for this tube. The discharges triggered in the tube are amplified in V and counted by the scale-of-D D and the mechanical register E. The deflection of the mA-meter F is proportional to the frequency of the discharges.](image)

involved a number of successive samplings and exposures. In general, one to three hours was required before any resulting data could be utilized.

Considerable improvement was achieved by substituting a photoelectric Geiger counter tube for the photographic plate as a means for detecting the energy of the spectral line at 2203 Å. In fact, this line, if isolated by a spectrograph, can be measured by a radiation detector, such as the Geiger tube, and the information concerning other spectral


A few details of the apparatus used, which was constructed for E. I. du Pont de Nemours & Co. by Philips Laboratories at Irvington, N.Y., are described here 4).

The complete set-up is shown in figs 2 and 3. A slit which can be moved across the spectrum is mounted in the focal plane of the quartz spec—

The spectrograph which disperses the radiation from the spark source. The position and width of the slit are adjusted so as to let only the 2203 Å lead line pass.

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**Fig. 3.** Photograph of exit slit assembly with Geiger counter tube and preamplifier, at the back of the spectrograph. By the micrometer screw at the right the slit position in the spectrum may be adjusted.

The Geiger counter tube is placed behind the slit. Between the axial wire anode and the surrounding cylindrical cathode of this tube a voltage of about 1500 V is applied. Short discharge pulses are triggered in the tube by the photo-electrons liberated from the cathode metal by the ultraviolet radiation impinging on the inside wall. The radiation enters the cathode cylinder through a rectangular slot cut lengthwise in the wall as shown in **fig. 4.** The discharge pulses are amplified and fed to a mechanical counter or to a circuit measuring the rate of arrival of the quanta at the counter tube by the mean value of a current. The circuits used for this purpose are similar to those used in the Geiger counter X-ray spectrometer described earlier in this Review 5).

The deflection of the rate meter milliammeter provides a direct check on the lead concentration at the place where the air is pumped off to the spark. It is possible to make a continuous record of this concentration if desired, or to make the instrument sound an alarm as soon as the lead content exceeds a given limit. The whole apparatus including the power supplies is mounted on wheels so that every part of the manufacturing area can be surveyed. The spectrograph and the counter tube with a pre-amplifier are mounted in an airtight box in which an inert atmosphere can be maintained, in case the air of the area to be examined should contain some inflammable vapor. The spark source is mounted in an air duct which traverses the airtight box. Air is forced through the duct by a small fan driven by an explosion-proof motor. To prevent a “flash-back”, which may occur in case of an explosion, fire screens are mounted on the intake and outlet of the air duct.

The fact that the Geiger tube in this application serves as a photo-electron counter entails several peculiarities in its design not encountered in the more common counter tubes intended to respond to electrons, gamma-rays or X-rays. In X-ray applications, for instance, the counter tube must be designed to absorb the entering X-rays in the gas volume between the electrodes, the absorbed X-ray quanta setting electrons free (cf. the article quoted in 5)); the choice of the electrode metal is not important in this case. In the photo-electron counter, however, the gas filling must be chosen so as not to absorb any of the entering ultraviolet radiation quanta, because such an absorption would not in all cases give rise to a discharge pulse, and the cathode must be made of a metal giving a strong photoemissive effect. In our case a very pure (O.F.R.C.) copper cathode, cleaned by prolonged heating in hydrogen, was used. The energy necessary for liberating an electron from this metal amounts to \( E = 4.42 \text{ electronvolt} \); hence, according to Einstein’s law, the maximum wavelength capable of liberating an electron, given by \( \lambda = \frac{hc}{E} \) (where \( h \) = Planck’s constant) is about 2800 Å. This shows that the counter tube will be sensitive in the spectral region with which we are concerned. The anode is a tungsten wire 75 μ in diameter. The electrodes are mounted in an envelope of clear fused quartz and the tube is filled with argon at a

pressure of 20 cm Hg. A small amount of alcohol vapor is added for rapidly quenching the discharge (cf. 5)). Neither of these gases absorbs the 2203 Å line to an appreciable extent. The counters have proved very reliable during their rated lifetime, so that during the past three years the instrument has been kept in almost continuous operation.

In the spectrograph (a Hilger E3), the rays of every wavelength converge onto their respective places in the focal plane in beams comprising an angle of about 10 to 30°, while the focal plane itself is situated obliquely to these beams; cf. fig. 5. As a consequence the radiation of the line 2203 Å, passing through the slit, is contained in a beam of a rather unfavorable configuration to be caught in the counter tube. A simple solution for this difficulty, avoiding the necessity of a rather artificial tube design, was found by mounting a mirror of stainless steel on the back of the slit, in the manner shown in fig. 5. When the angle of the mirror is adjusted to a suitable value, all the radiation passing through the slit is reflected into the hole of the counter cathode. The reflectivity of steel (and most other materials) for the ultraviolet radiation of 2203 Å is rather poor at normal incidence, but at grazing angles of incidence as occur in our case, practically complete reflection of the radiation is obtained.

![Fig. 5. Geometrical configuration of the beam of radiation of 2203 Å arriving at the exit slit of the spectrograph. By a mirror M of stainless steel mounted on the back of the slit, the entire beam is reflected into the hole of the counter tube cathode.](image)

Once in several months it is necessary to scan the spectrum on either side of the lead line 2203 Å for readjustment of the slit. The adjacent copper lines are easily located, whereupon the slit is set on the lead line position by a simple interpolation. Of course, on moving the slit across the spectrum the configuration of the beam reflected by the mirror will change to some extent. The hole in the counter tube cathode wall is made large enough to receive the whole of the reflected beam for all positions of the slit within the portion of the spectrum which it may be desired to scan. The alignment of the spectrograph with the source, of course, must be checked more frequently, viz., once or twice during an eight hour period, as it is not possible for a simple portable instrument to maintain good optical alignment for a longer period under plant conditions. Every now and then the overall stability and sensitivity of the apparatus may be checked by measuring the relative intensities of the 2200 and 2195.8 Å copper lines.

A chart of the spark spectrum, as determined by setting the slit in subsequent positions about 1/2 Å apart and noting the number of counts per second, is shown in fig. 6a. Fig. 6b gives a microphotometer trace of a photograph of the spectrum taken with the same spectrograph. The resolution of lines in the two cases is almost identical and more than adequate to resolve the 2203 Å lead line from nearby copper lines. A striking difference between the two spectra is the much lower background of the counter tube trace. This is due to the fact that the counter, because of the photoelectric threshold, is not affected by scattered radiation of wavelengths longer than 2800 Å arriving at the slit, whereas the photographic plate responds to this radiation.

The low background sensitivity of the Geiger counter tube is important, both for a practical and a fundamental reason.

In the photographic method, where the whole spectrum is recorded, the background contribution to the plate density can be recognized as such on inspection of the plate and appropriate corrections made. So the background does not prevent a very feeble line from being observed, and after corrections for the background have been applied a fairly accurate quantitative evaluation of the lead concentration from the relative line intensities is possible.

With the direct indicating Geiger counter method, however, no information is available during normal operation as to whether the measured number of counts per second is due to the lead line or to the background. The presence of the lead line must be derived and its intensity (L) evaluated by subtracting a constant number of counts (B), ascribed to the background and obtained as a result of a zero experiment, from the total number (B+L). In view of the statistical character of the arrival of radiation quanta at the counter tube, this total number contains a probable error \( \sqrt{B + L} \), which in full is transmitted to the result, L, of the subtraction. The relative error \( \sqrt{B + L}/L \) can be made small enough only by prolonged
counting. Obviously, the necessary counting time for a given accuracy will be shorter the smaller the background intensity \( B \). This will be especially important when the counting rate (intensity \( L \)) is low.

![Fig. 6](image)

**Fig. 6.** (a) Copper spectrum, determined by measuring the number of counts per second for a large number of positions of the exit slit (about \( \frac{1}{2} \) Å apart). The position of the lead line 2203 Å is indicated by a dotted line.

(b) Microphotometer trace of copper spectrum obtained photographically.

This is a practical consideration. A fundamental one is that, in reality, even the statistical mean value \( B \) is not a constant; the background is subject to continuous changes due to the erratic behaviour of the spark discharge. These changes have much more influence with the Geiger tube than with the photographic plate, owing to the shorter averaging time. By the uncertainty of the value of \( B \) to be subtracted, a lower limit of the detectable lead concentration is imposed. So it may be said that the low background sensitivity of the counter tube is chiefly responsible for the comparatively high lead sensitivity of the apparatus. The lower limit of detectability, in a single measurement, is about 0.6 mg lead per m\(^3\) air, or 1 part in about 2 million on a weight basis. Although this sensitivity cannot compete on equal terms with that of the photographic method, it is fully adequate for the purpose of leak hunting, where the discovery of local variations in lead concentration is all-important.

Several years' experience has shown the inherent soundness of the method for the detection of lead. However, it should be emphasized that in the construction of the apparatus there is little that points to its specificity for lead. The flexible hose and other tubing are made of "Saran" (a plastic) instead of rubber because certain lead compounds have a high affinity for rubber. The mirror behind the slit is specifically adjusted for the 2203 Å position of the slit. Apart from these minor details, there appears to be no fundamental reasons why the instrument could not be used for the detection of other elements, provided these elements show a sensitive emission line in a suitable spectral region and the slit is placed in the correct position. The analysis of dusts for elements such as arsenic, barium and beryllium are suggested examples.

Using a more constant source and a more elaborate technique, spectrochemical analysis with the Geiger counter is also feasible in cases where accurate quantitative data are required, as was shown in recent publications concerned with the analysis of the phosphor content of steel \( 6 \). The background difficulties mentioned previously can be obviated by a method of "internal control", similar to the one used in the photographic procedure: by using two Geiger counter detectors it is possible to measure the ratio between the intensities of the lead line and an adjacent copper line, and thereby average out fluctuating background. Though, in some situations, also in our case accurate quantitative data may be desired, the method of internal control was discarded in the instrument described, as it would have unnecessarily complicated the instrument for the purpose of leak hunting; in a specific case it is easy enough to obtain quantitative information from a photographic recording of the spectrum.


**Summary.** A spark discharge is maintained between two copper electrodes in the air of a plant where atmospheric contamination with lead or lead compounds can occur through possible leaks in plant installations. If lead is present the
spark will contain the lead line at 2203 Å. By a small quartz spectrograph provided with a movable slit in its focal plane, this spectral line is isolated and its intensity is measured by a photoelectric Geiger counter tube with counting rate meter. The sensitivity of the apparatus in normal operation is limited to about 0.60 mg lead per m$^3$ air, by the fluctuations of the background intensity emitted by the spark. Although this is more than the maximum permissible concentration of lead in the air (0.15 mg per m$^3$), the instrument has proved very useful as a means for detecting and locating small leaks in pipes or valves, in whose vicinity high lead concentrations may occur. The superiority of the method as compared with the usual and more sensitive photographic procedure of spectrochemical analysis is due to the fact that the direct indicating, continuous working, radiation meter is ideal for monitoring changes in concentrations.

**ABSTRACTS OF RECENT SCIENTIFIC PUBLICATIONS OF THE N.V. PHILIPS' GLOEILAMPENFABRIEKEN**

Reprints of these papers not marked with an asterisk can be obtained free of charge upon application to the Administration of the Research Laboratory, Kastanjelaan, Eindhoven, Netherlands.


A new type of betatron is described in which the magnetic field is obtained by means of coils in air, through which the discharge current of a 6.5 μF condenser battery passes. There is only a small iron core, by means of which it is easy to fulfil the “flux condition”. Saturation of the core effects contraction of the orbits towards the end of the acceleration period, until the electrons strike a tungsten target 0.1 mm thick. The betatron as a whole weighs no more than 50 kg, the iron core itself weighing less than 5 kg. The peak value of the magnetic induction is 0.4 Wh/m$^2$ (4,000 gauss), the radius of the orbit 8 cm; the energy of the accelerated electrons amounts to 9 MeV. Cf. Philips Techn. Rev. 11, 65-78, 1949 (No. 3).

1858: J. A. Haringx: Het merkwaardig gedrag van op druk belaste schroefveren (Voor- drachten Kon. Inst. Ingenieurs 1, 298-313, 1949, No. 3). (The remarkable behaviour of compression-loaded helical springs; in Dutch.)

A survey is given of the remarkable phenomena demonstrated by compression-loaded helical springs in respect of their elastic stability, lateral rigidity and natural frequencies for transverse vibrations. The existence of these phenomena was predicted on account of a theoretical calculation which was based upon the current simplification of replacing the helical spring by an elastic prismatic rod and a new interpretation of the latter’s rigidity against shearing. At the end of the paper it is shown that the respective problems had to be treated first before helical springs could successfully be applied as resilient elements for vibration-free mountings.

1859: J. L. Snoek: Time effects in ferromagnetism (Physica ’s Grav. 15, 244-252, 1949, No. 1/2).

In an attempt to give a short systematic survey of time effect in ferromagnetism a distinction is made between effects involving structural charges of the lattice (ionic time-effects) and effects affecting only the conditions of the 3d- and 4s-electrons (electronic time-effects). The ionic effects may be divided into time-effects involving plastic deformations, time-effects involving interstitial diffusion and effects of unknown origin (in ferrites). The electronic time-effects may be divided into eddy-current effects and ferromagnetic resonance effects.


In connection with an article of Levine and Schwinger on the diffraction of a scalar plane wave by an aperture in an infinite plane screen, the writer briefly indicates the derivation of the correct expression for the transmission coefficient of a circular aperture.

1861: G. W. Rathenau: Enige nieuwe resultaten op het gebied van rekrystallisatie (De Ingenieur 61, Mk 57-Mk 63, 1949, No. 20). (Some new results on recrystallization; in Dutch.)

Some recent views on recrystallization. Review of recent literature on polygonization, recrystallization and grain growth. Some new results concerning the secondary recrystallization of nickel-iron alloys are discussed.