A SPECTROGRAPHIC STUDY OF ULTRA-VIOLET FLUORESCENCE EXCITED BY X-RAYS

By J. O. Perrine

Abstract

Fluorescent spectra excited by x-rays.—(1) *Ultra-violet.* In order to photograph the spectrum, the specimen being studied was placed in front of the slit of a Fuess single-prism quartz spectrograph and was exposed to x-rays from a Coolidge tube with the target about 12 cm off. With the tube operating at .002 amp. and 50 kv and a slit width of .15 mm, exposures up to 15 hours were made. *Over one hundred substances* were tested. Fourteen double salts of uranium, 23 oxides, 50 other compounds and also anthracene, chrysoidine, eosin and fluorescine gave no ultra-violet fluorescence, though some show brilliant bands in the visible; but positive results were obtained with *the chlorides of Cd, Cs, Li, K, Na, and Rb, and also with KBr, KI,* $BaSO_4$, $RaSO_4$ *and* $CaWO_4$. NaCl gave a strong band with maximum at 2470A and CsCl gave a band extending from 5720 to 2340A with three maxima. Several willemite screens, some x-ray intensifying screens and one fluoroscopic screen also showed ultra-violet fluorescence. The intensity of fluorescent response decreased for successive exposures. (2) *Visible fluorescence.* One or more bands in the visible were emitted by all the salts showing ultra-violet fluorescence, except barium and radium sulfates, and also by ZnO, CdI, Cu_2I_2 and HgCl and, of course, by the uranyl salts.

Changes of color of chlorides due to x-rays.—RbCl was observed to turn dark blue, NaCl buff, KCl and LiCl pink, and CsCl blue. The original white color was restored by exposure to sunlight, but did not return in the dark. This change may be due to a reduction to the metal and Cl, which is then occluded. The salts had been carefully purified.

Photo-electric photometer for measuring distribution of density in a spectrogram is described. A Kunz cell was used.

If x-radiation, which is of the order of one angstrom in wavelength is used as the incident radiation, one would expect in accordance with Stokes' law that, in addition to the fluorescent radiation produced in the visible region, fluorescence in the ultra-violet region might be produced.

The first study of the production of ultra-violet fluorescence by x-rays was made by Winkelman and Straubel.[1] In the case of fluorspar, they report a band of fluorescent radiation extending from 3,960A to 2,330A with a maximum of 2,800A. Schuhknecht[2] examined spectrographically

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[1] Winkelman and Straubel, Wied. Ann. 1896

[2] Schuhknecht, Ann. der Phys. **17**

the fluorescence emitted from a number of natural minerals and inorganic compounds under x-ray excitation. The following substances are reported by him to give fluorescent radiation of wave-length less than 4000A; fluorspar, two samples; uranium ammonium fluoride, and scheelit.

The fluorescent materials used in x-ray fluoroscopic and intensifying screens were studied by Hodgson.[3] When excited by x-rays, these substances gave evidence of fluorescence in the ultra-violet. According to his work, the fluorescent radiation from calcium tungstate extends to approximately 3650A.

Apparatus and Experimental Procedure

The substance under examination was placed in front of the slit of a Fuess spectrograph[4] with the surface of the specimen at an angle of 45° with the vertical face of the collimator head. The x-ray tube was placed directly above the specimen so that the x-rays passed through the top of a light-tight box fastened to the end of the collimator. By this arrangement all extraneous light was excluded. The distance from the specimen to the x-ray target was approximately 12 cm.

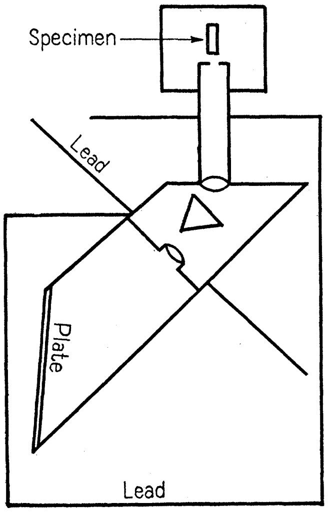

Fig. 1. Optical system.

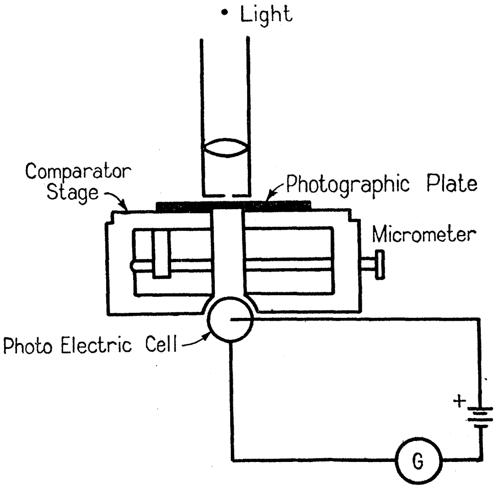

Fig. 2. Photo-electric spectro-photometer.

Fig. 1 shows the general arrangement of the optical system. The plate holder could be moved in a plane perpendicular to that of the figure, and exposure could thus be obtained at various places on the same photographic plate. A Stanley plate, 6 by 9 cm, was used.

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[3] Hodgson, Phys. Rev. **12**, 431 (1918)

[4] Zeit. für Instrumentenkunde **28**, 34. Instrument used is referred to as No. 3

A quartz mercury arc lamp was used to obtain a calibration spectrum on the photographic plate directly above and below the fluorescent spectrum. The intensity of the fluorescent radiation was so small that an exposure of several hours was necessary even though a slit width of .15 mm was used.

As a source of x-rays, a radiator type Coolidge tube was used with a current of two or three milliamperes at 50,000 volts.

In taking photographs under the conditions described, it was found that diffusely scattered x-rays caused the plate to be badly fogged even though the x-ray tube was provided with the usual lead glass shell directly about the bulb. Protection from these scattered x-rays was secured by lead screens made of two layers of 1/16-inch thick lead. In some plates, a shadowgraph of a small metal clip on the rear side of the plate holder was obtained. This particular circumstance together with the general fogging indicated very definitely that diffuse x-radiation came from the brick wall situated about three feet away from the rear side of the spectrograph and the x-ray tube. It was found necessary to surround the spectrograph completely by these lead plates, and in the final arrangement, satisfactorily clear negatives were obtained even after exposures of fifteen hours.

Photo-electric photometer for measuring the blackening of the photographic plate. Fig. 2 shows the general arrangement of the apparatus. The eye piece, cross hair and objective of the comparator telescope were removed, leaving only the telescope tube. A 100-watt, single coil filament lamp was mounted on the telescope tube at the upper end. A lens placed within the base of the tube focused the light from the lamp on a slit at the center of a metal plate fitted in the lower end of the tube. The slit was .25mm wide and 2mm high and was usually lowered to within .5mm of the surface of the plate, which was placed on the comparator stage. The light which was transmitted by the small area of the plate in front of the slit, entered the photo-electric cell. Proper precautions were taken to keep out all extraneous light.

The Elster and Geitel type of photo-electric cell was first tried, but the leakage current, or so-called dark current observed was so large that reliable results could not be obtained. The Kunz[5] photo-electric cell was, however, found to be very satisfactory. When 120 volts were used, the dark current seldom exceeded 2 per cent of the maximum light current, and after the circuit had been closed for 15 minutes it decreased to .5 per cent of the maximum light current. Within the light-tight box containing the photo-electric cell a beaker of concentrated sulphuric acid

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[5] Kunz and Stebbins, Phys. Rev. **7**, 282 (1916)

was placed to assist in decreasing the leakage over the surface of the cell.

A Leeds and Northrup type "C" galvanometer (sensibility 11900 megohms) was used, and the entire arrangement was so sensitive that the 100-watt lamp could be operated at 15 per cent below normal rating, and only 55 volts need be applied to the photo-electric cell. The incandescent lamp and the photo-electric cell were operated by separate storage batteries. Observations showed that a change in the potential used in the photo-electric cell circuit did not change the relative value of reading throughout some particular fluorescent band.

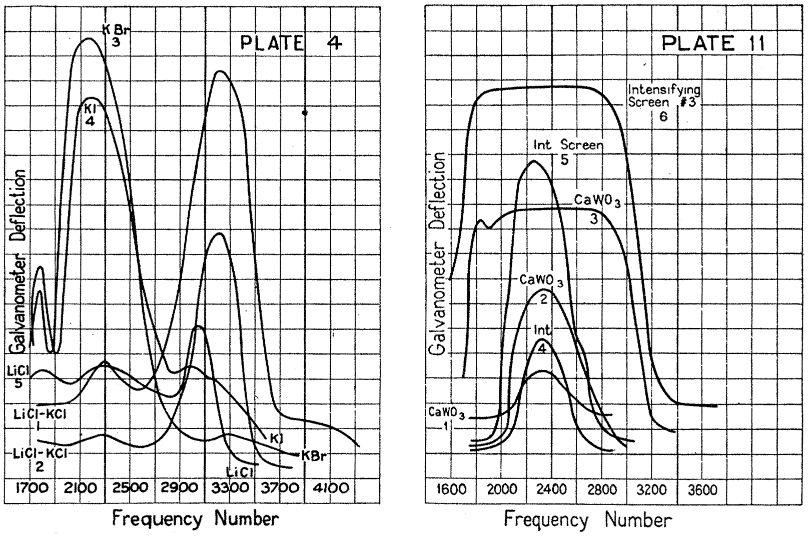

Fig. 3. Blackening distribution curves.

PLATE 4

Curve 1. Recrystallized mixture LiCl-KCl—10 hours' exposure
Curve 2. Recrystallized mixture LiCl-KCl— 4 hours' exposure
Curve 3. Potassium bromide — 4 hours' exposure
Curve 4. Potassium iodide —14 hours' exposure
Curve 5. Lithium chloride — 6 hours' exposure

PLATE 11

Curve 1. Calcium tungstate — 1-min. exposure
Curve 2. Calcium tungstate — 2-min. exposure
Curve 3. Calcium tungstate —30-min. exposure
Curve 4. Intensifying screen #3— 1-min. exposure
Curve 5. Intensifying screen #3— 2-min. exposure
Curve 6. Intensifying screen #3—30-min. exposure

FLUORESCENT SPECTRA

The experimental results are given in Figs. 3–6 and in Tables I and II. In the blackening distribution curves, galvanometer deflections are used as ordinates, and are referred to the upper left-hand corner of the page as the origin of axes. Frequency numbers, i.e., the reciprocals of wave-length in centimeters, are used as abscissae.

CHANGE OF INTENSITY OF FLUORESCENCE UNDER CONTINUED ACTION OF X-RAYS

In the early part of the work, several samples of willemite, which gave positive results, were subjected to repeated exposures for checking purposes. These samples gave fluorescence of decreasing intensity under these repeated exposures. Two samples, particularly, which had given fine blackening of the plate at a region corresponding to 3560A, later gave very faint blackening in this region. Other conditions were thought to be the same, in fact, the intensity of the x-radiation was greater in the later tests than in the former ones. These two samples were again exposed after two months' time. They failed to show any recovery during this interval.

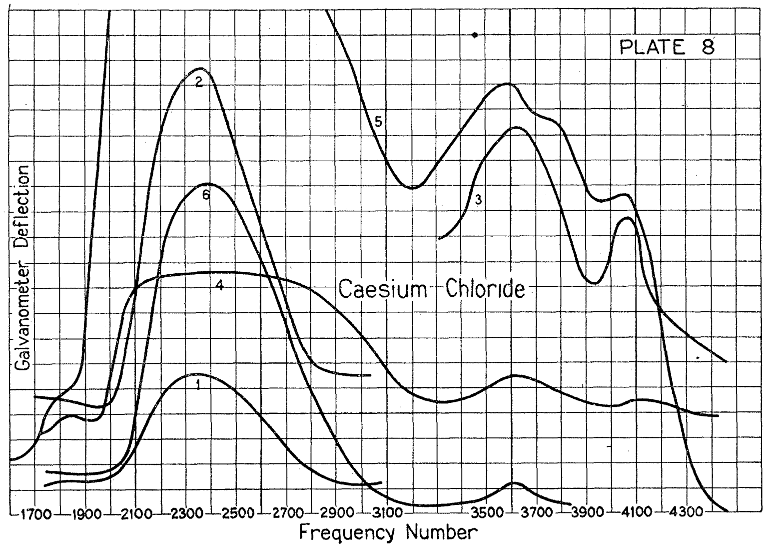

Fig. 4. PLATE 8

Curve 1.	6-minute exposure
Curve 2.	20-minute exposure
Curve 3.	5-hour exposure with microphotometer at high sensibility to bring out second and third bands
Curve 4.	3.5-hour exposure with microphotometer at low sensibility
Curve 5.	5-hour exposure with microphotometer at high sensibility
Curve 6.	30-minute exposure to bring out second band faintly

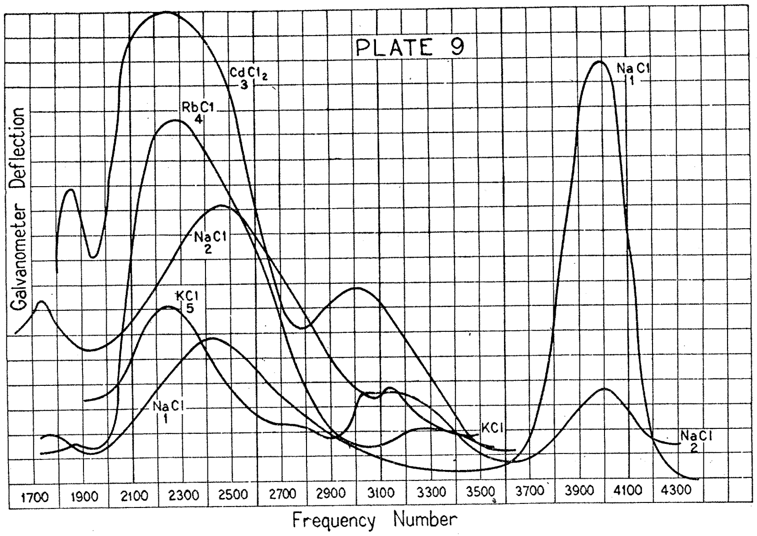

Fig. 5. PLATE 9

Curve 1. Sodium chloride —15-hour exposure—Sample #1
Curve 2. Sodium chloride — 8-hour exposure—Sample #2
Curve 3. Cadmium chloride — 5-hour exposure
Curve 4. Rubidium chloride—12-hour exposure
Curve 5. Potassium chloride— 8-hour exposure

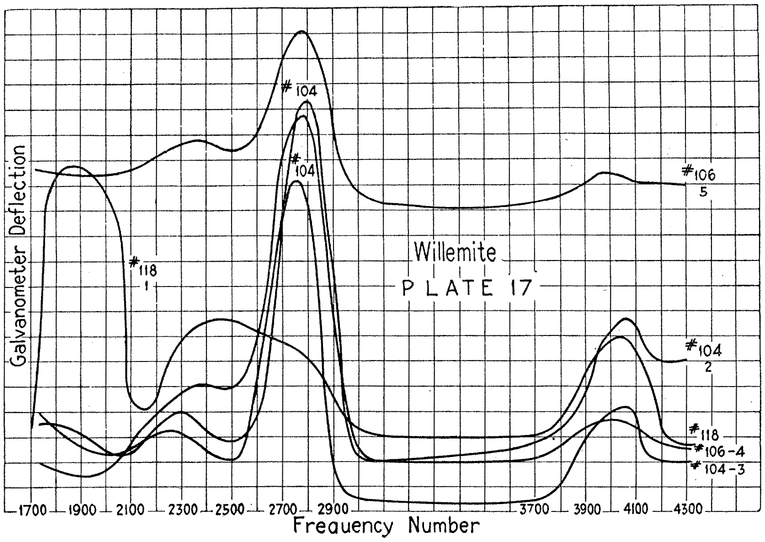

Fig. 6. PLATE 17. Willemite

Curve 1. Number 118—7.5-hour exposure
Curve 2. Number 104— 7-hour exposure—Sample #1
Curve 3. Number 104— 7-hour exposure—Sample #2
Curve 4. Number 106— 11-hour exposure—Sample #1
Curve 5. Number 106— 11-hour exposure—Sample #2

TABLE I. COMPOUNDS SHOWING NO ULTRAVIOLET FLUORESCENCE

The number following each salt indicates the number of hours exposure to x-rays.

Uranyl Compounds

Ammonium potassium uranyl chloride (5)
*Barium uranyl acetate (12)
*Caesium uranyl chloride (12)
*Cadmium uranyl acetate (8)
*Lead uranyl acetate (12)
*Lithium uranyl acetate (10)
*Mercuric uranyl nitrate (8)
*Potassium uranyl acetate (3)
*Rubidium uranyl nitrate (5)
*Rubidium uranyl sulfate (5)
*Silver uranyl nitrate (13)
Strontium uranyl acetate (2)
Thallous uranyl sulfate (8)
Uranyl tellurate (13)

Oxides

Aluminum oxide (5)
Antimony oxide (12)
Barium oxide (10)
Bismuth oxide (10)
Berylium oxide (6)
Cadmium oxide (6)
Calcium oxide (12)
Calcium peroxide (5)
Cuprous oxide (5)
Cupric oxide (5)
Erbium oxide (10)
Germanium oxide (5)
Magnesium oxide (8)
Magnesium peroxide (5)
Silicon oxide (12)
Silicon dioxide (10)
Strontium oxide (6)
Strontium peroxide (5)
Tin oxide (12)
Uranium oxide (15)
Uranium peroxide (18)
*Zinc oxide (8)
Zinc peroxide (8)

Miscellaneous Compounds

Anthracene (5)
Barium chloride (5)
Berylium chloride (5)
Cadmium bromide (5)
Cadmium fluoride (5)
[1]Cadmium phosphate (5)
[1]Cadmium sulfide (5)
Caesium aluminum sulfate (5)
Caesium di-chor-iodide (5)
Calcium Sulfide (10)
Chrysoidine (5)
Copper selenate
Cupric bromide (7)
Cupric sulfide (5)
Didymium chloride (7)
Eosin (crystal) (5)
Fluorescine (5)
Indium iodate (5)
[3]Iron pyrites (5)
Magnesium perborate (4)
Mercuric chloride (5)
Mercuric copper iodide (7)
Mercuric iodide (7)
Mercuric sulfide (5)
Molybdenic acid (5)
[3]Molybdenite (6)
Potassium auri bromide (5)
Potassium cuprisulfide (7)
Potassium fluoride (4)
Potassium fluotitanate (5)
Potassium periodate (7)
Rochelle salts (5)
Rubidium di-chor-iodide (5)
[2]Silver bromide (5)
[2]Silver chloride (5)
Silver dichromate (5)
[2]Silver iodide (5)
Silver mercuric iodide (7)
Sodium boro-fluorate (5)
Sodium fluoride (5)
Sodium periodate (5)
Sodium silicate (5)
[3]Stibnite (5)
Strontium chloride (5)
Sulfur (block) (10)
Telluric acid (5)
Thallium bromide (5)
Thallium chloride (5)
Thorium nitrate (5)
Tin chloride (5)
Tungstic acid (5)
Zinc (sheet) (5)
Zinc bromide (4)
[1]Zinc sulfide (12)

*Give narrow fluorescent bands in the visible.

[1] Reported by Dr C. W. Waggoner as highly purified and not fluorescent under excitation by ultra-violet light.

[2] These three silver salts had been freshly prepared and kept from ordinary light at all times.

[3] These three sulfides were large crystals with flat mirror-like surfaces.

TABLE II. COMPOUNDS WHICH GAVE POSITIVE RESULTS

Substance	Frequency number limits of band	Frequency number of maximum	Time of exposure to x-rays
Barium sulfate	2000–3700	2610	6 hours
Barium sulfate Radium sulfate	2100–3200	2750	12
Cadmium chloride		See Plate 9, Fig. 5	
Cadmium iodide	1700–1950 2000–2400	1810 2190	5
Caesium chloride		See Plate 8, Fig. 4	
Calcium tungstate		See Plate 11, Fig. 3	
Cuprous iodide	2100–2450	2300	10
Lithium potassium chloride (Chemical Dept. sample)	2800–2880 2880–3600	2840 3220	12
Lithium potassium chloride (50–50 mechanical mixture)	2000–2600 3000–3600	2220 3220	4
Lithium potassium chloride (50–50 recrystallized mixture)		See Plate 4, Fig. 3	
Lithium chloride		See Plate 4, Fig. 3	
Mercurous chloride	1750–1850	1800	5
Potassium bromide		See Plate 4, Fig. 3	
Potassium iodide		See Plate 4, Fig. 3	
Potassium chloride		See Plate 9, Fig. 5	
Rubidium chloride		See Plate 9, Fig. 5	
Sodium chloride		See Plate 9, Fig. 5	
Willemite 104		See Plate 17, Fig. 6	
Willemite 118		See Plate 17, Fig. 6	
Willemite 106		See Plate 17, Fig. 6	
X-ray intensifying screen No. 3 (Patterson)		See Plate 11, Fig. 3	
X-ray fluoroscopic screen No. 1 (Patterson)	1600–2780 1700–1900 1900–2600 1800–2500	Flat 1800–2320 1810 2190 2210	5.5
Zinc oxide	1700–1850 1950–2300	1775 2070	5

In the case of all the samples of artificial willemite which gave positive results, three fluorescent bands were present. In some samples the band in the visible was very faint, while in other samples the two ultra-violet bands were very faint. In all cases where the far ultra-violet band was strong enough to permit of measurement, the maximum blackening of the plate checked at a frequency number of 4050. All of the samples of artificial willemite had been made by Mr D. T. Wilber of the Physics Department, Cornell University.

In considering these curves, it will be noticed that the points of maxima for potassium iodide and potassium bromide are almost exactly at the same frequency number. However, cuprous iodide has a maximum at 2300, which is the same as one of the maxima for potassium bromide and iodide. Potassium chloride has a maximum at 2250, while lithium chloride has a maximum at 2290. Caesium chloride has one of its maxima at 2340. Sodium chloride and caesium chloride each has a band at a point located at about 4000. Caesium chloride gave most beautiful photographic records of ultra-violet fluorescence. The two maxima in the ultra-violet are very readily seen by visual inspection of the original negative. The fluorescence extends very definitely out to 2250 A.

CHANGE IN COLOR DUE TO EXPOSURE TO X-RAYS

In connection with these experiments, some marked color changes were observed. Highly purified rubidium chloride, which is a white salt, became a dark blue, looking very much like a piece of copper sulphate. This color change was observed after an exposure of five hours. The photographic plate gave evidence of both visible and ultra-violet fluorescence. It was then a question whether or not this specimen already a dark blue, would fluoresce upon further excitation by x-rays. It was found to fluoresce as strongly as before. Upon removing the specimen and exposing it to ordinary day-light, the original whiteness returned within three hours.

A sample of highly purified sodium chloride turned to a marked buff color. The original whiteness of the salt was not restored in three days. Potassium chloride and lithium chloride became pink under the action of x-rays. In these two cases the original color returned within an hour. Potassium bromide took on a light blue and potassium iodide a brown-buff color. Caesium chloride turned to a dark blue and returned within an hour. As in the case of rubidium chloride, caesium chloride, which had been turned blue by exposure to x-rays, was tested again and fluoresced equally well during the second exposure. To determine whether there might be some fluorescent radiation emitted during the time in which the original white color was returning, the substance was left in the light-tight box, the photographic plate moved to a different exposure surface and a 36-hour exposure taken. At the end of this time, the specimen was still as blue as at the beginning and no evidence of fluorescence appeared on the plate. It was found on exposure to daylight that the substance turned white within five minutes.

It is not unlikely that these color changes were due to a reduction of a small fraction of the chloride into the metal concerned and free chlorine. The chlorine, perhaps, is retained by adsorption in the unreduced portions. The entire mass appeared to be changed in color but it is very possible that the reduction of a small amount is sufficient to give color to the entire mass. Exposure to light appears to be necessary in order to reverse the change. The fact that a specimen exposed once gave further fluorescence on a second exposure, would not necessarily indicate that the fluorescence did not accompany the color change. As stated above, a small amount of reduced salt might color the entire mass so that during the exposure the continual reduction might occur with resulting fluorescence. To the eye, however, no additional color changes took place.

Whenever the specimen, after an exposure, showed a color change the developed plate gave evidence of ultra-violet fluorescence except for silver bromide, silver iodide and silver chloride. The color changes in these three salts were much less than had been expected since they show marked color changes when exposed to ordinary daylight.

The rubidium, potassium, and sodium chlorides had been carefully prepared[6] and were highly purified as far as the presence of other metals was concerned. Spectroscopic examination confirmed the absence of calcium and magnesium.

In conclusion, the writer wishes to express his appreciation for the kindly interest and encouragement of Professor Ernest Merritt under whose direction the work was done. For advice and suggestions given by other members of the Department of Physics, the writer is also indebted.

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[6] The actual preparation was made by Dr Papish of the Chemistry Department, Cornell University.