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SUBJECT: Flame Photometric Determination of Iron
Parts I, II, III and IV

TO: See Distribution

FROM: Oscar Menis

TCR-26 through 29
OM-37 through 40

ABSTRACT

A study was made of a method for the flame photometric determination of iron. In Part I of this report, the flame emission spectrum of iron, measured by means of a Beckman Model DU spectrophotometer with a flame attachment, is compared to that measured with an ORNL high-sensitivity, recording, single-beam instrument, in order to determine which instrument is best suited for this application. Although it was found that the Beckman product has the higher resolving power over the wavelength region of 360 to 400 mμ, it does not possess the sensitivity or ease of operation of the ORNL instrument. On this basis, the ORNL flame spectrophotometer is used in subsequent tests. After selecting the best-suited instrument for the flame photometric determination of iron, it was necessary to establish the optimum operating conditions for this particular method. These conditions are described in Part II.

Further tests were carried out to establish the extent to which 17 elements and 10 anions interfere in this method (Part III). Milligram quantities of Sb(V), Cr(VI), Mo(VI), and Sn(IV) were found to interfere as does Th in high concentrations. This latter interference can be eliminated by a washing technique. Of 10 anions tested, nitrate and perchlorate interfere even in very low concentrations, while acetate, citrate, and phosphate can be tolerated when present in moderate amounts. In Part IV, the precision of the method for the determination of iron in slurries of thorium oxide and other materials is discussed. The limit of error of the method is within 10 per cent.

DISCLAIMER

FLAME PHOTOMETRIC DETERMINATION OF IRON

Part I: Flame Emission Spectrum of Iron

T. C. Rains
Oscar Menis

Purpose

To decide, from flame emission spectral data, which of two flame photometers, the Beckman DU spectrophotometer with flame attachment or the ORNL flame photometer, is best suited for use in the flame photometric determination of iron in hexone solutions and to select the optimum wavelength at which to measure the radiant intensity of the iron.

Introduction

The present investigation has been made to compare the flame emission spectrum of iron as recorded by two different instruments, the Beckman DU and the ORNL flame spectrophotometer.(2) Since the ORNL flame spectrophotometer uses a grating monochromator and the Beckman DU a prism, it is of interest to make a comparison of the two spectra and determine which instrument is best suited for the flame photometric determination of iron. While the flame emission spectrum of iron has been reported by several workers,(1,3) only Dean and Lady(1) have attempted to use an organic solvent in the flame photometric determination of iron. They made use of acetylacetone which served as the chelating agent and also the solvent, but they failed to report the spectrum of iron from an acetylacetone medium. The major difference between spectra from aqueous and organic media is the occurrence of CH or C_2 bands in the latter. These bands constitute a major interference at certain regions of the iron spectrum. Since hexone offers advantages over acetylacetone, as described in a previous report,(4) the present study is limited to this medium.

Reagents

See ORNL CF-59-3-106.

Apparatus

Oak Ridge National Laboratory, high-sensitivity, recording, single-beam flame spectrophotometer, Model No. Q-1457A, equipped with an RCA (6217) multiplier phototube.(2)

Beckman Model DU spectrophotometer equipped with a multiplier phototube, 1P28, voltage control, and a Beckman flame photometer attachment, Model 9290.

Experimental

A solution of iron that contained 100 µg of iron was transferred to a 30-ml separatory funnel. After the addition of 5 ml of hydrochloric acid, the sample was diluted to 10 ml with water. Ten ml of hexone was added and the separatory funnel was slowly shaken for 30 seconds. After the phases had separated, the organic phase was removed and aspirated into the oxyhydrogen flame of the instruments. The radiant intensity was measured over the wavelength range of 365 to 400 mµ. The radiant intensity over this range is presented graphically in Figures 1 and 2 for the Beckman DU and ORNL flame spectrophotometers, respectively.

Discussion

The flame emission spectrum of iron is characterized by a series of lines with the major peaks at 372.0, 373.7, 374.7, and 386.0 mµ, as shown in Figure 1. The iron doublet of 373.7 and 374.7 mµ is not resolved in the ORNL flame spectrophotometer and appears as one line at a wavelength of 374 mµ as shown in Figure 2. Since this line is a sum of two lines, it is stronger than either the 372- or the 386-mµ lines of iron. The reproducibility of the line at 374 mµ is very erratic because of this unresolved grouping and a base line technique has to be used to determine the background. However, this line serves as a guide in the identification of the iron lines at 372 and 386 mµ. In the Beckman DU, the two lines at 373.7 and 374.7 mµ are resolved, but they are of little interest since they are not as sensitive as the other major iron lines.

The iron line at 372 mµ will be used for future study as it is more intense than the 386-mµ line and the background radiation at 370 mµ is more constant in comparison with the background radiation in the vicinity of the 386-mµ line. The background for the 386-mµ line measured at 382 or 385 mµ is erratic because of the interference from a weak iron line at 384 mµ. The iron line at 386 mµ can be used, if desired, and would certainly have to be utilized if tin, ruthenium or magnesium were present because they either have lines or bands at a wavelength of 372 mµ.

The two instruments differ in that with the Beckman DU, greater resolution can be attained, but with the ORNL instrument a gain in sensitivity is achieved because it is equipped with a more sensitive multiplier phototube detector. The background radiation for both instruments is essentially the same over the wavelength region of 365 to 390 mµ and is characterized by a strong CH band at a wavelength of 390 mµ.

Conclusion

A comparison was made of the flame emission spectrum of iron in hexone when measured by means of the Beckman DU and ORNL flame spectrophotometers. The Beckman DU is observed to have higher resolving power, but it does not possess the sensitivity of the ORNL instrument. The Beckman DU spectrophotometer is converted to a flame spectrophotometer with attachments while the ORNL instrument is designed for use in flame photometry and therefore is more convenient to operate. While an instrument with high resolution is a desirable asset when spectral interferences are encountered, the more selective extraction of iron from other interferences obviates this need. On the other hand, by means of the ORNL instrument, greater sensitivity and ease of operation is achieved. Therefore, the ORNL instrument will be used for future studies in the flame photometric determination of iron.

For the reasons set forth in the discussion, 372 mμ was selected as the optimum wavelength for measuring the radiant intensity of iron in hexone solutions. If elements which interfere at this wavelength, such as tin, ruthenium or magnesium, are present, the measurement can be made at 386 mμ or even at 384 mμ, with appreciable loss of sensitivity.

References

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ORNL-LR-DWG. 38265

FLAME EMISSION SPECTRUM OF IRON IN HEXONE

(Fe, μg/ml --- 10)

BECKMAN DU FLAME SPECTROPHOTOMETER
VOLTS / DYNODE, ------ 65
SLIT WIDTH, mm ---- 0.03

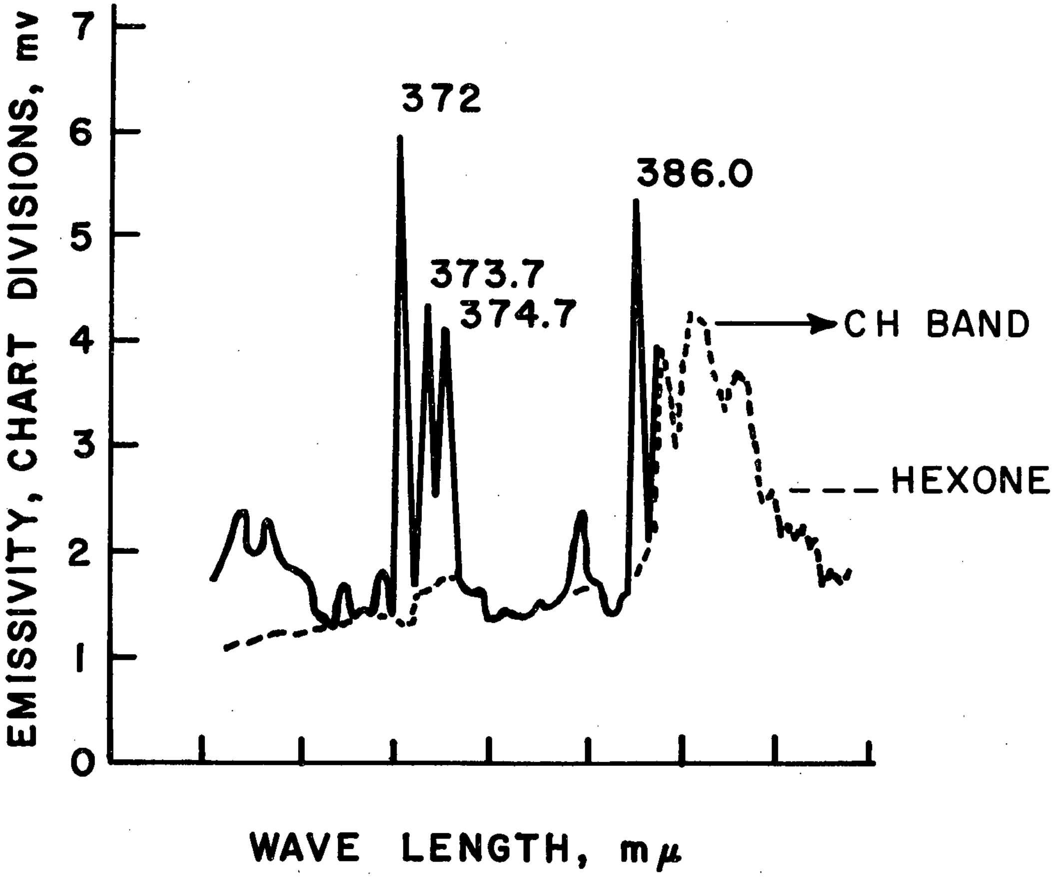

FIGURE 1 -- PART 1

Fig. 2

PART I

FLAME EMISSION SPECTRUM OF IRON IN HEXONE

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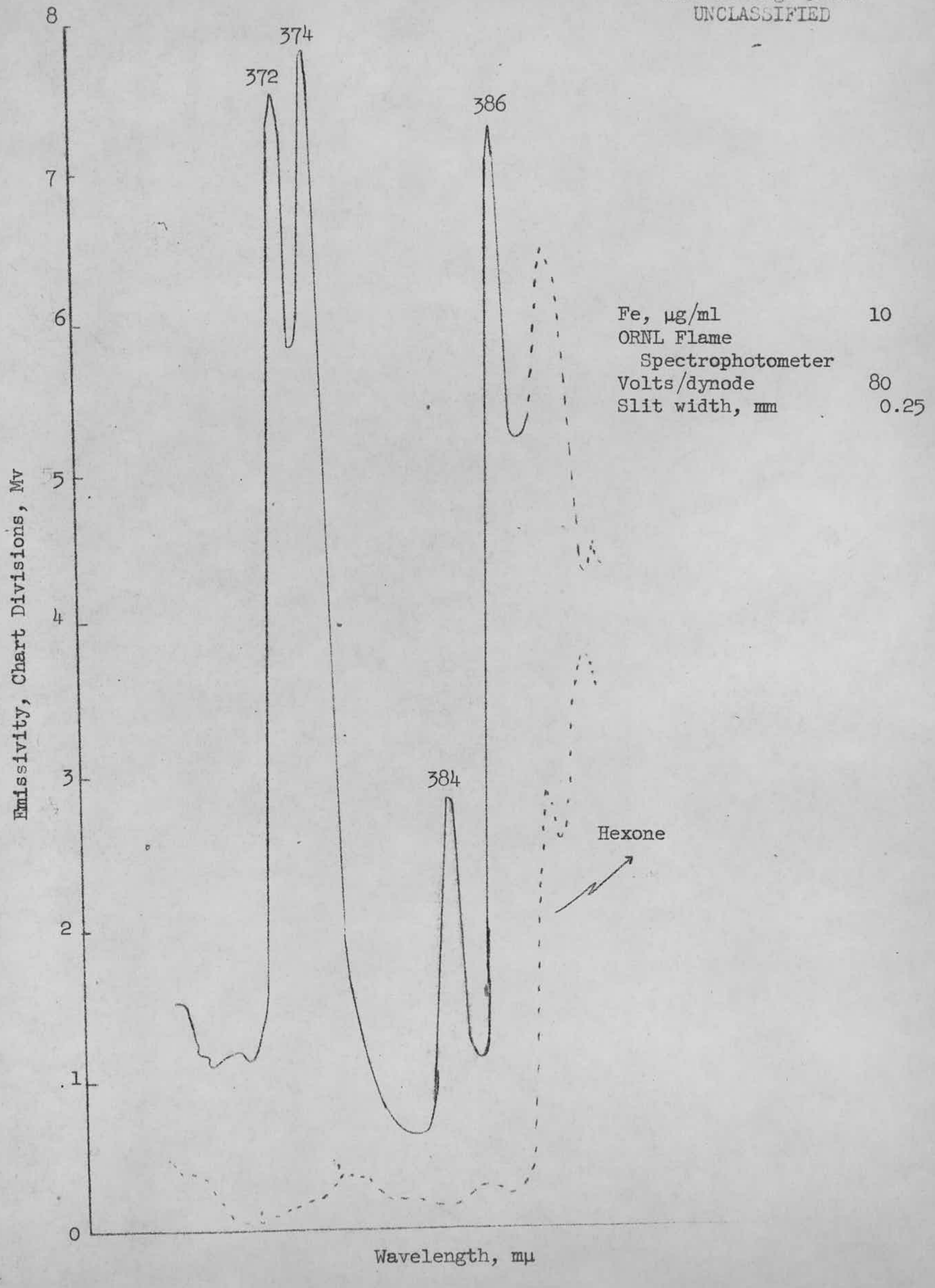

Part II: Evaluation of Operational Conditions and Establishment of a Calibration Curve

Purpose

To evaluate the effect of instrumental variables on the selectivity and reproducibility of the flame photometric method for the determination of iron, to establish optimum operating conditions, and to prepare a calibration curve for iron under these conditions.

Introduction

In the flame photometric determination of iron, as well as of other elements, optimum operating conditions must be empirically established. These include variables such as choice of solvent, wavelength, fuel and gas pressure, slit width and other instrumental settings. The conditions thus selected govern the sensitivity, reproducibility, degree of linearity of the calibration graph, and freedom from interference from other substances. It is essential, therefore, that proper conditions be selected.

Since each element responds differently to the variations of fuel and oxygen pressures,(8) failure to operate at optimum gas pressures for a given element will affect the sensitivity. The ensuing decrease in sensitivity can be in part overcome by choosing wider slit widths. The selection of slit width, however, is controlled by the proximity of the spectral line or band to be used for the emissivity measurement to spectral lines or bands of other elements present in the test solution. Sufficient resolution must be provided so that the radiant intensity of the element to be determined alone is measured (unless a standard addition procedure is utilized). If no lines or bands of possible interfering substances are near the line or band used for the emissivity measurement, or, if the sample is essentially free of interferences, a wide slit width can be used to advantage to attain greater sensitivity.

In flame photometry the selection of solvents plays an important role since the medium in which the element is present affects the rate of aspiration, size and stability of flame, and background radiation. Also, the selection of a proper organic extraction medium may aid substantially in eliminating a large number of interferences.

A study was made of the effects of conditions such as: optimum fuel and oxygen pressure, slit width, multiplier-phototube stability, scanning rate. In addition, three solvent media, dilute HCl, acetylacetone and hexone were investigated. Finally, a calibration curve was established for use when iron is aspirated in an hexone medium.

Apparatus

Instrument: Oak Ridge National Laboratory, high-sensitivity, recording, single-beam flame spectrophotometer, Model No. Q-1457A, equipped with an RCA 6217 multiplier phototube and a modified Beckman DU atomizer-burner.

The atomizer-burner was modified by removing the lacquer from the adjusting screws which control the flow to the palladium capillary. The adjusting screws were then silver soldered. This modification was made to insure that the burner would function properly when organic solvents were aspirated into it.

Experimental

To establish the optimum gas pressure, a solution that contained 10 μg of iron per ml in hexone was prepared as described in Part I. While maintaining the oxygen pressure constant and varying the hydrogen pressure, the hexone solution was aspirated into the flame and the radiant intensity of the iron was measured at 372 mμ. This technique was repeated for various oxygen pressures ranging from 6 to 14 psi. The data were then plotted as shown in Figure 1.

After the optimum gas pressures were established for the determination of iron, the effect of slit width was evaluated by scanning the flame emission spectrum of iron over the wavelength range of 360 to 390 mμ. The data are presented in Figure 2.

To ascertain the effect of the wavelength scanning speed, the emission spectrum of iron was recorded using scanning speeds of 11, 22, and 44 mμ per minute, as shown in Figure 3. Since the ORNL instrument(5) is equipped with a Minneapolis-Honeywell Brown motor No. 77311-2, these scanning speeds are controlled by using the following combination of gears; 80T-40T, 60T-60T, and 40T-80T, respectively.

The relative sensitivity of iron was then determined for three media: 0.1 N HCl, acetylacetone, and hexone. To secure a sample of iron in acetylacetone, the medium used by Dean and Lady,(3) a one-ml aliquot of an iron standard, 500 μg/ml, was transferred to a 50-ml beaker and diluted to 10 ml with water. After adjusting the pH of the sample to one with dilute hydrochloric acid it was transferred to a 30-ml separatory funnel. Then, 10 ml of acetylacetone was added and the separatory funnel was shaken for one minute. When the two phases had separated, the aqueous phase was withdrawn into a clean separatory funnel. The extraction was repeated with four, successive 10-ml portions of acetylacetone. The organic phases were then combined in a 50-ml volumetric flask and diluted to the calibrated volume with acetylacetone. The hexone solution was prepared by extracting iron as described in Part I. The emissivity of the iron in each of the three media was then determined under identical operating conditions with the exception of the fuel and oxygen pressure. The latter was adjusted for each solvent to yield maximum emissivity for iron. In order to establish the linearity

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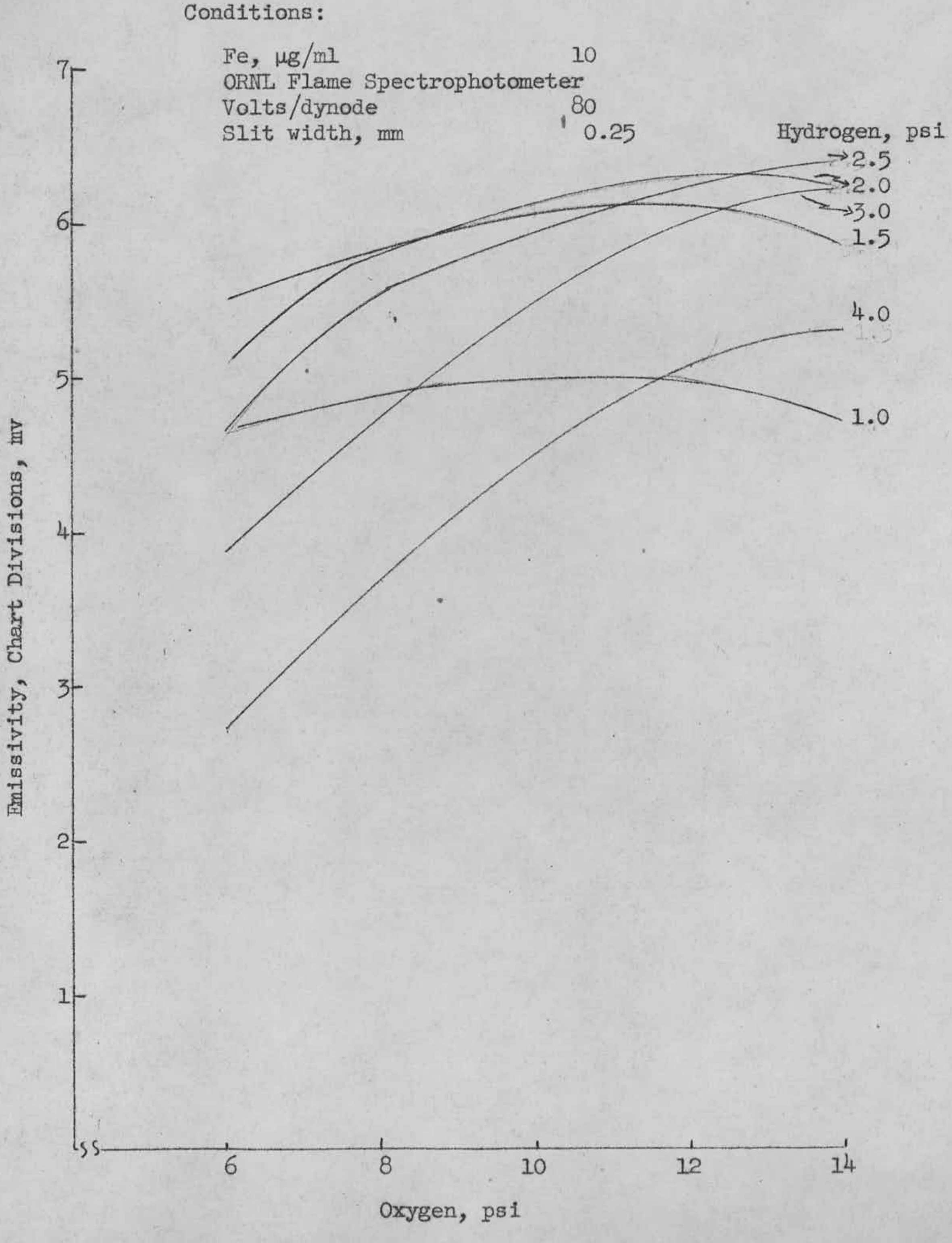
Figure 1

PART II

Emission of the 372-mμ Iron Line for Various Oxygen and Hydrogen Pressures



Conditions:

Fe, μg/ml	10
ORNL Flame Spectrophotometer	
Volts/dynode	80
Slit width, mm	0.25

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Fig. 2

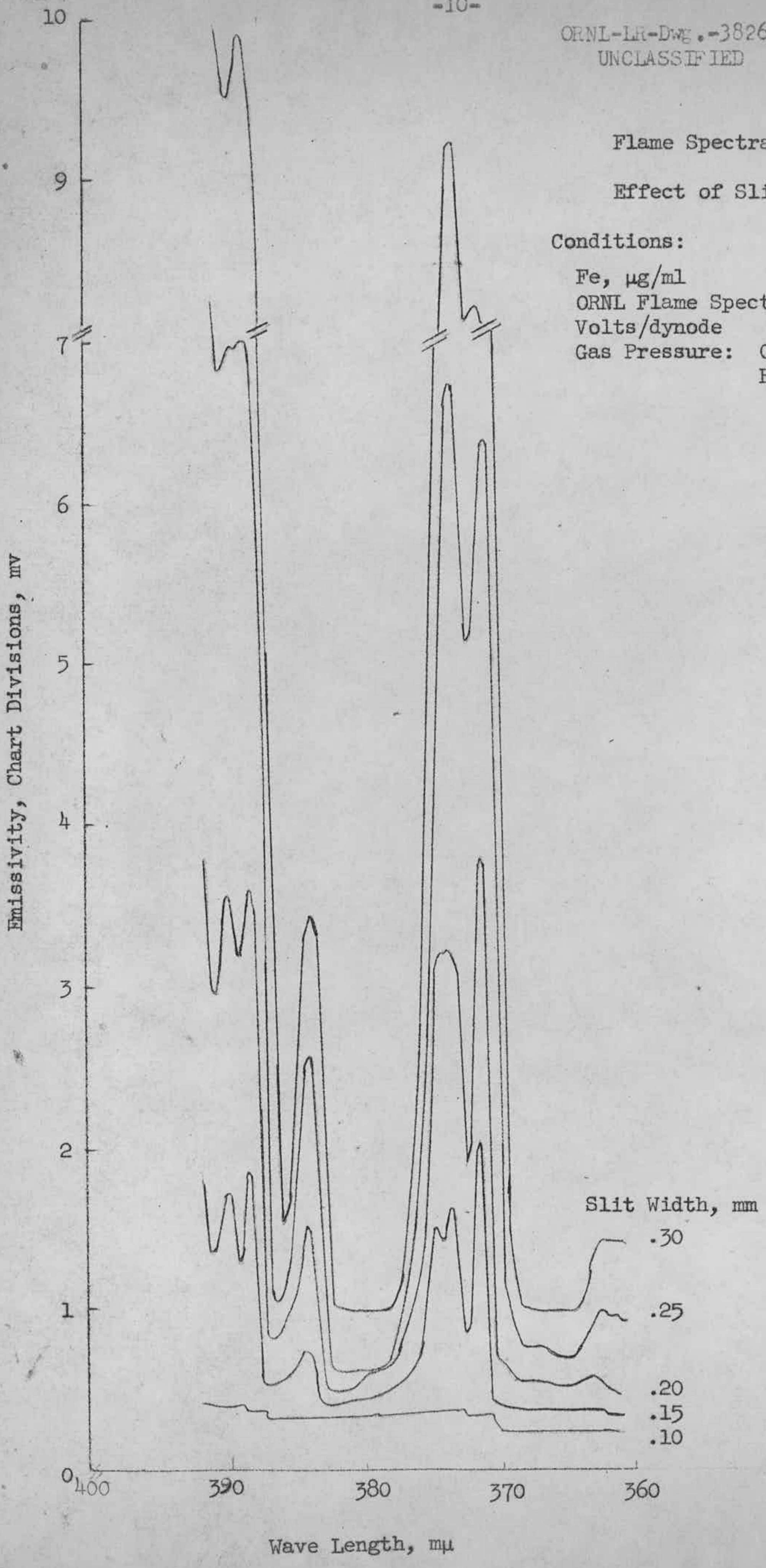
PART II

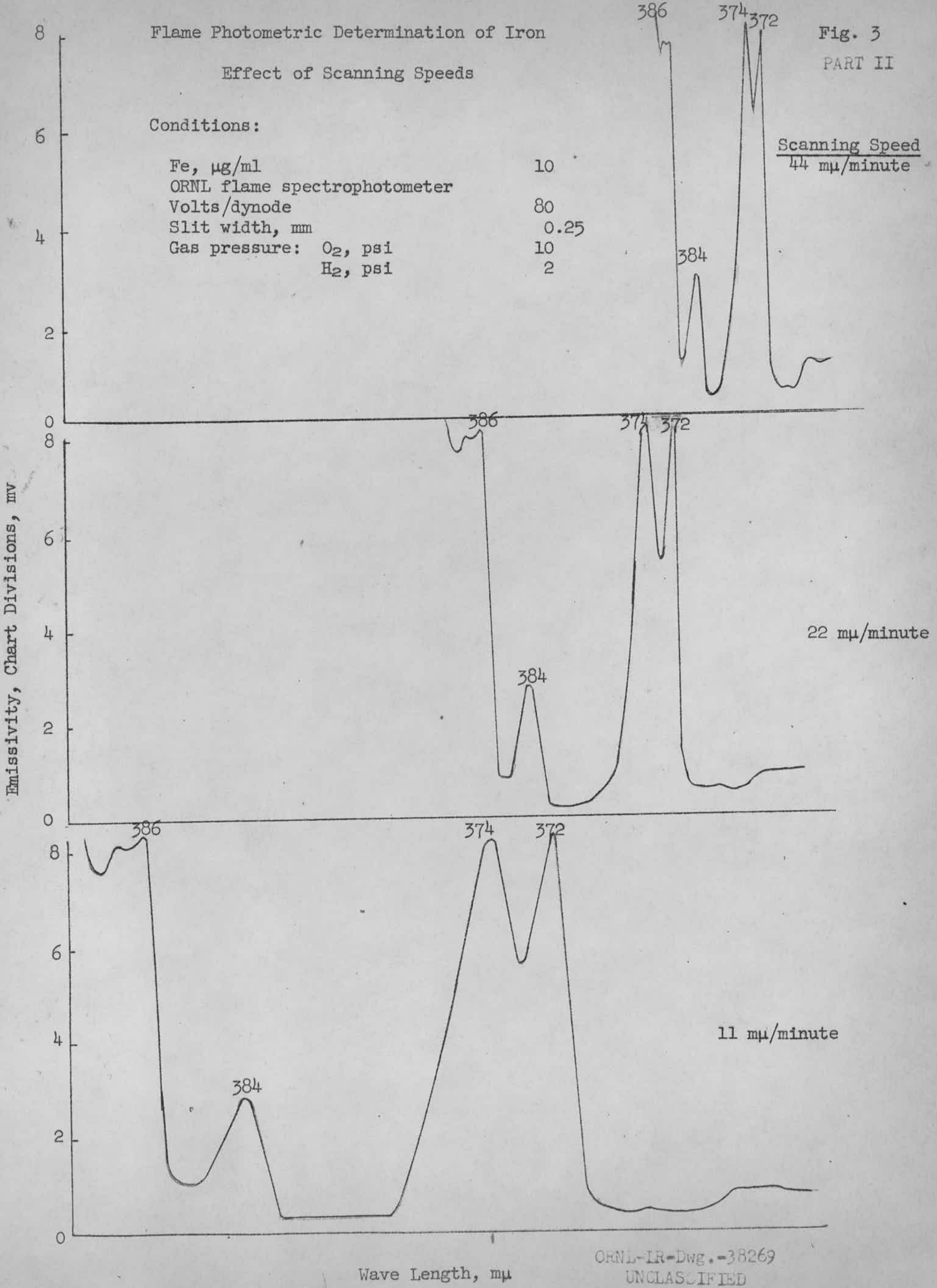
Flame Spectra of Iron

Effect of Slit Width

Conditions:

Fe, µg/ml		10
ORNL Flame Spectrophotometer		
Volts/dynode		80
Gas Pressure:	O_2, psi	10
	H_2, psi	2





Flame Photometric Determination of Iron

Effect of Scanning Speeds

Conditions:

Fe, μg/ml	10
ORNL flame spectrophotometer	
Volts/dynode	80
Slit width, mm	0.25
Gas pressure: O_2, psi	10
H_2, psi	2

Fig. 3

PART II

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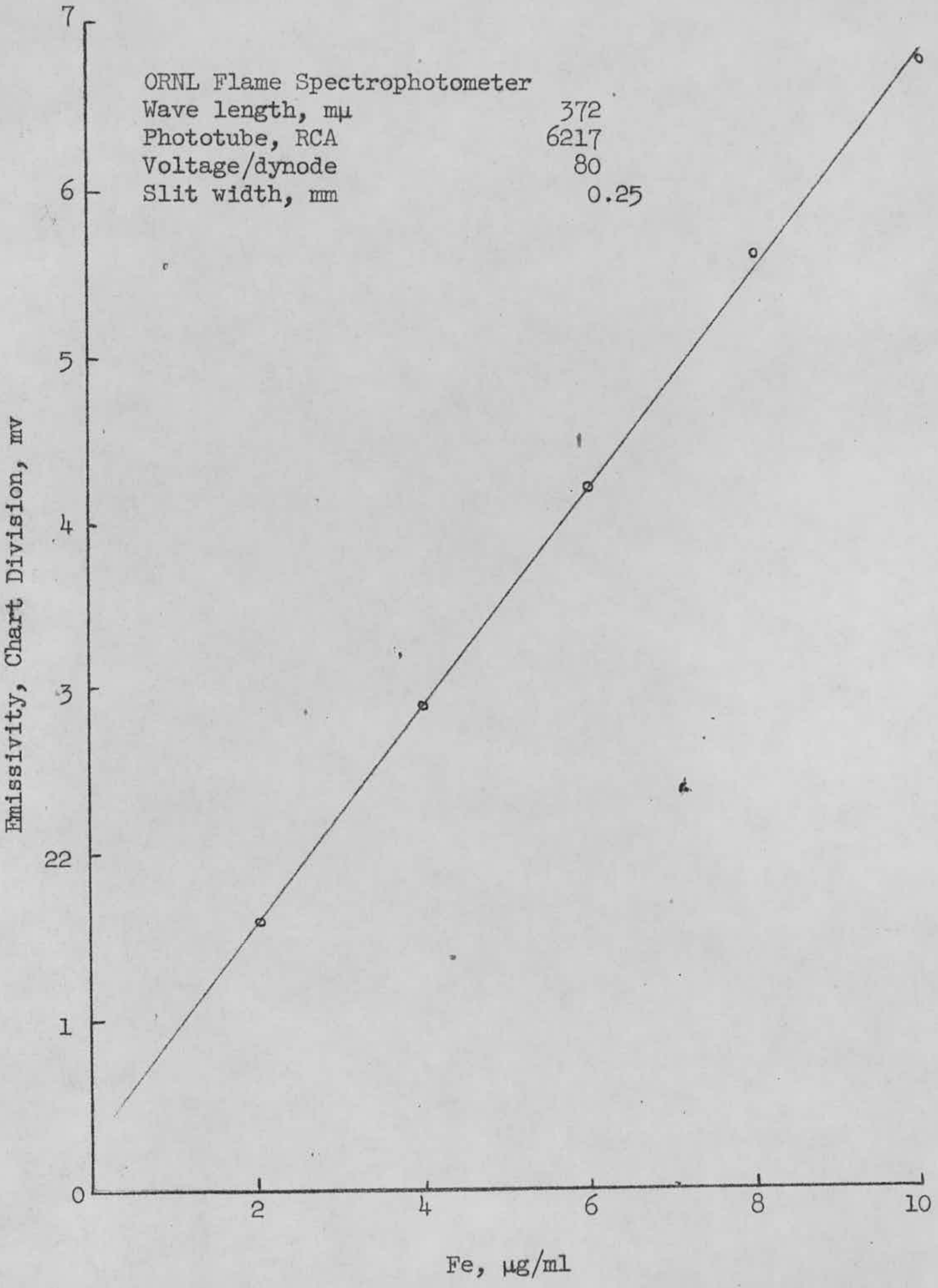
Fig. 4

PART II

Calibration Curve for the Flame Photometric Determination of Iron in Hexone



of the calibration curve of iron in a hexone medium, a series of samples was prepared that contained from 2 to 10 μg of Fe per ml. The radiant intensity of the iron at a wavelength of 372 mμ was measured and plotted versus the concentration as shown in Figure 4.

Discussion

The optimum pressures of hydrogen and oxygen for maximum emissivity and stability of the Fe-372 mμ line were found to be 2 and 10 psi, respectively, as shown in Figure 1. With the oxygen pressure set below 8 psi, the rate of aspiration was irregular and therefore the emissivity became erratic. The emissivity increases slightly with increased oxygen pressure. Optimum oxygen pressure is in the range of 10 to 12 psi. The hydrogen pressure was found to have a more pronounced effect on the emissivity of the iron than the oxygen pressure. With an oxygen pressure of 10 psi, the emission of the iron increased with increasing hydrogen pressure until a pressure of 2 psi was attained; then a sharp drop in emissivity was observed with increasing hydrogen pressure. This sharp drop of emissivity is believed to be due to a change in the volume of the flame and the region from which light is focused on the phototube. Normally, at an optimum hydrogen pressure, light from the hotter portion of the flame which is above the inner cone reaches the phototube. However, as the hydrogen pressure is increased the flame becomes larger until, at 6 psi, it extends above the chimney and the inner cone is elongated until it extends to a height of 4 cm. Light focused on the phototube now comes from the cooler region of the flame containing the inner cone. Since emissivity is a function of flame temperature, the emissivity decreases abruptly when the hydrogen pressure becomes great enough to project the inner cone into the region from which the phototube receives light.

The choice of slit width will be governed by the degree of reproducibility and sensitivity desired, and by the number, type and concentration of interferences present. Since relatively few elements are extracted into hexone, and of those which are extracted, still fewer interfere specifically with the measurement of the emissivity of iron at 372 mμ, the criteria for the selection of slit width in the flame photometric determination of iron may be, for practical purposes, limited to the attainment of the desired sensitivity and reproducibility. The effect of variation in slit width is presented in Figure 2. While a slit width of 0.30 mm yields the greatest sensitivity, it leads to loss of resolution of the 372-, 373.7- and 374.7-mμ lines of the flame spectrum of iron. For the estimation of iron based on emissivity measurements at 372 mμ, a slit width of 0.3 mm is undesirable because the two adjacent lines coalesce with the 372-mμ line. The three spectral lines can be resolved by the use of a slit width of 0.15 mm but with a considerable loss of sensitivity. In order to attain the maximum sensitivity possible and at the same time resolve the 372-mμ line, a slit width of 0.25 mm was selected and used in the measurement of the emissivity.

Of the three media studied, dilute HCl, acetylacetone and hexone, the hexone yields the highest sensitivity for the estimation of iron, as shown in Table I. Dean and co-workers(2,3) have reported on the use of HCl and acetylacetone for the flame photometric estimation of iron. While the sensitivity obtained with acetylacetone is of the same magnitude as that with hexone, the former reagent is severely limited in its application. For example, in the extraction of 500 μg of iron with acetylacetone, five extractions are required for the quantitative removal of iron. Also, acetylacetone is appreciably miscible with water and the flame is erratic unless an additional filtration is carried out to remove water from the organic phase. Finally, with acetylacetone, even at pH 1 rather than a pH of 3 at which iron is more completely extracted, the extraction is less selective than with hexone.

Part II: Table I

Effect of Media on the Flame Photometric Determination of Iron

Conditions:		
	ORNL flame spectrophotometer	
	Multiplier phototube, RCA	6217
	Volts/dynode	80
	Slit width, mm	0.25
	Gas pressure: Oxygen, psi	10
	Hydrogen, psi	2

Medium	Fe, μg/ml	Scale Division	Fe, μg/ml/ Scale Division	Sensitivity Ratio Aqueous/Organic
Hexone	2*	60	0.03	-
	10	75	.13	10
Acetylacetone	10	52	.19	7
HCl, 0.1 N	20	16	1.25	1

* Volts/dynode = 100

While the relative intensities of the emissivity for a given element can be readily ascertained, the absolute value can vary considerably as determined by different laboratories for specific instruments and flame burners. With the ORNL flame photometer(5) which is equipped with an RCA 6217 multiplier phototube with an applied voltage of 100 V per dynode and slit width of 0.25 mm, the maximum sensitivity that was attained in a hexone medium was 0.03 μg per ml per scale division. Under similar conditions but with the lower voltage per dynode of 80, the sensitivity drops to 0.13 μg per ml per scale division. The maximum voltage at which the phototube may be operated is 120 V per dynode, but at this voltage the instrument response is erratic.

The ORNL instrument is also equipped with an interchangeable gear mechanism for varying the scanning rate. The results for scanning rates of 11, 22 and 44 mμ per minute are presented in Figure 3. When narrow slit widths are required, the slowest scanning rate yields more reproducible data. On the other hand, with broad emission bands, the highest speed of 44 mμ can be used. In the determination of iron a scanning speed of 22 mμ per minute yields the desired resolution and reproducibility.

The calibration curve was found to be linear over the concentration range tested; that is, from 2 to 10 μg of iron per ml at a wavelength of 372 mμ.

Conclusion

The operating conditions for the flame photometric determination of iron by means of the ORNL flame spectrophotometer were investigated. It was found that the optimum conditions for the ORNL instrument are: gas pressures, oxygen, 10 psi and hydrogen, 2 psi; slit width, 0.25 mm; and a scanning speed of 22 mμ per minute. Under these conditions the calibration curve for the iron 372-mμ line is linear over the concentration range tested, 2 to 10 μg Fe/ml, and the maximum sensitivity attainable is 0.03 μg/ml/scale division. It was also found that hexone increases the emissivity of iron by a factor of 10 over that of an aqueous solution, while acetylacetone increases it by a factor of seven. The use of hexone has certain distinct advantages over acetylacetone. It extracts iron much more effectively; only a single extraction is required. Furthermore, the emissivity of iron in hexone is about 40 per cent greater than in acetylacetone and the hexone flame is more stable than the corresponding flame with acetylacetone.

References

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8. H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, _Instrumental Methods of Analysis_, D. Van Nostrand, New York, 1958, pp. 233-249.

Part III: Interferences of Various Elements and Anions

Purpose

To evaluate the interference of various elements and anions in the flame photometric determination of iron in a hexone extract.

Introduction

It has been established that iron can be separated from numerous other components and concentrated by extracting it from a strongly acidic solution (6 M HCl, preferably) with hexone, after which it can be determined in the organic extract by flame photometry. (See Part II, TCR-27.) The extent to which many elements and anions encountered, especially in slurries of thorium oxide and other materials composing the major sample types submitted for analysis in conjunction with HRP corrosion test and engineering development work, interfere with the flame photometric determination of iron had not been evaluated. Accordingly, a series of interference tests was made and the results are reported herein.

Experimental

A series of test solutions was prepared that contained 6 μg of Fe per ml and the elements or anions to be tested for interference in various concentrations. The iron was extracted with hexone as outlined in Part II. The radiant intensity of the iron in the organic (hexone) extract was then measured by means of a flame photometer at a wavelength of 372 mμ. A calibration graph for iron was prepared at the same time and the amount of iron extracted was determined by referring the radiant intensity observed to the calibration graph, after which the per cent extracted was computed. The test results are presented in Tables I and II.

Discussion

Of the 17 elements investigated, only Sb(V), Cr(VI), Mo(VI) and Sn(IV), at the concentrations tested, were found to interfere with the flame photometric determination of iron. Although Sb in low concentration, 0.1 mg per ml, can be tolerated, larger amounts cause the results for iron to be low. Chromium(VI) extracts with the iron and enhances the radiant intensity. As much as 5 mg of Cr per ml can, however, be tolerated if the Cr(VI) is reduced to Cr(III) with hydroxylamine hydrochloride. Molybdenum and tin are also extracted with hexone from a HCl solution and they greatly enhance the intensity of the 372-mμ line in the emission spectrum of iron. The enhancement "of molybdenum" is due to continuous radiation, whereas the tin produces a series of oxide bands in the region of 372 mμ. By utilizing a narrow slit, e.g., 0.2 mm, and a wavelength of 386 mμ for measurement of the radiant

Part III: Table I

Interference of Various Elements in the Flame Photometric Determination of Iron

Fe, µg/ml 6

Element	Concentration, mg/10 ml	Iron Found Per Cent
Antimony, Sb	1	100
	20	83
Boron, B	10	96
Cobalt, Co	50	98
Chromium, Cr(VI)	5	105
Cr(III)	50 (NH_2OH-HCl added to reduce Cr(VI))	100
Copper, Cu	10	98
Molybdenum, Mo	1	101
	10	123
Palladium, Pd	10	102
Ruthenium, Ru	10	102
Silicon, Si	10	97
Tin, Sn	1	103
	2	117
	5	133
	5 (Slit: 0.2 mm)	110
Titanium, Ti	4	100
Thorium, Th	100	91
	300	68
	300+	100
Uranium, U	90	96
Vanadium, V	3	100
Zinc, Zn	10	98

\+ Organic phase washed with HCl-HF solution

Part III: Table II

Effect of Extraneous Anions in the Flame Photometric Determination of Iron

Conditions:	Fe, µg/ml	6
	ORNL Flame Spectrophotometer	
	Multiplier phototube, RCA	6217
	Volts/dynode	80
	Slit width, mm	0.25

		Iron Found, Per Cent	
Anion	Concentration, M	No Washing	After Washing*
Acetate	1.0	93	98
Citrate	0.5	88	100
EDTA	.3	97	
Fluoride	.01	98	
	.1	98	
	1.0	98	
HEDTA	0.3	101	
Nitrate	.01	90	99
	.1	88	93
	.5	65	79
Perchlorate	.01	93	99
	.1	84	90
	.5	13	66
Phosphate	.5		97
	1.0	75	96
	3.0		92
Sulfate	0.05	100	
	.75	97	
	1.0	95	
Tartrate	0.5	100	

* Organic phase washed with 10 ml of 6 M HCl prior to measurement of radiant intensity.

intensity, the interference of tin at concentrations of 0.5 mg or less per ml can be reduced to a tolerable level. If the tin exceeds this concentration it is necessary to remove it prior to the determination of iron. This can be accomplished by volatilizing the tin as $SnBr_4$ from a sulfuric acid solution.(1)

Milligram quantities of thorium cause the results for iron to be low unless the organic extract is washed with a 6 M HCl solution which is also 0.1 M with HF. The HF is necessary to insure the removal of the last trace of thorium.

The washing of the organic (hexone) extract with 6 M HCl is recommended for any sample which contains other substances in high concentration. This is necessary because the aqueous phase is somewhat soluble in hexone. A significant amount of impurity present in high concentration will be carried into the organic phase and it may have a quenching effect on the emissivity. The washing step is for the purpose of removing objectionable substances prior to the measurement of radiant intensity.

Interference tests were made with 10 different anionic substances (see Table II). None of those tested inhibit the extraction of iron from 6 M HCl with hexone. This fact was established by extracting radioactive Fe^{59} from 6 M solutions containing each of the anions. In all cases, extraction of the iron was complete. Low test results for iron related to the presence of interfering anions can, therefore, be attributed to the quenching effect of the anion or anions on the emissivity of the iron.

Of the anionic substances tested for interference, sulfate, fluoride, tartrate, ethylenediaminetetraacetate (EDTA or Versene), n-hydroxyethylenediaminetriacetate (HEDTA or Versenol-120) did not, within the concentration ranges tested, interfere with the flame photometric determination of iron, even when the organic phase was not washed with 6 M HCl. The remaining anions tested, acetate, citrate, nitrate, perchlorate and, to a lesser degree, phosphate, did interfere by quenching the emissivity of the iron. The interferences of nitrate and perchlorate were especially severe; even in 0.01 M solutions of these anions, recovery of the iron was less than 80 per cent. In each case, the tolerance limit could be significantly increased by washing the hexone extract with 6 M HCl; however, even when this washing is made, the tolerance limit for nitrate and perchlorate is of the order of 0.1 M. As much as 1.0 M phosphate can be tolerated if a re-extraction is made.

Conclusion

Of 17 elements tested for interference in the method for the determination of iron, only Sb(V), Cr(VI), Mo(VI) and Sn(IV) were extracted with the iron and interfered with the subsequent flame photometric determination of iron. Methods are described for prevention of the interference of moderate amounts of Cr(VI) and small amounts of Sn. For thorium in high concentrations, the organic extract must be washed with a HCl-HF solution prior to the determination of iron flame photometrically. The washing procedure can also be used to increase the tolerance limits for acetate, citrate, nitrate, perchlorate and phosphate. No interference was observed for sulfate, fluoride, tartrate, EDTA and HEDTA, within the concentration limits tested (See Table II).

Future Work

Tests will be carried out to establish the precision of this flame photometric method for iron.

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Part IV: Precision of the Method

Purpose

To establish the precision with which iron can be determined in slurries of thorium oxide and other materials by a flame photometric method.

Introduction

Iron can be determined rapidly in slurries of thorium oxide and other materials by extracting it from a 6 M HCl solution with hexone, following which the concentration of the iron is established by aspirating the organic extract into a flame photometer, measuring the radiant intensity at 372 mμ, and referring the radiant intensity to a calibration graph (see Part II of this report for details of this procedure).

Experimental

Six replicate analyses were made by this flame photometric method to determine the concentration of iron in each of three National Bureau of Standards samples. Duplicate analyses were made also of two synthetic solutions, one of which contained thorium, the other uranium. The National Bureau of Standards samples differed widely as to type. A 2-gram sample of each (NBS No. 54b; 63a; 157) was dissolved in 20 ml of 6 N HCl plus a few drops of HNO_3. After the samples had dissolved, solutions of samples 63a and 157 were transferred to 50-ml volumetric flasks and diluted to volume with 1 N HCl. NBS sample No. 54b is a tin-base alloy; the tin was, therefore, volatilized as $SnBr_4$ from a H_2SO_4 solution after adding HBr.(1) Following removal of the tin, the sample was transferred to a 50-ml volumetric flask and diluted to volume with 1 N HCl. Aliquots of the three sample solutions which contained from 20 to 60 μg of iron were transferred to 30-ml separatory funnels and the iron was extracted with 10 ml of hexone as previously described in Part II. The hexone extracts were then analyzed flame photometrically for iron. The test results are set forth in Table I.

A synthetic solution was prepared which contained 10 mg of U, 0.5 mg of Cu, 0.0162 mg of Fe, 0.05 mg of Ni and 0.100 mg of Cr(VI) per ml. Also, a thorium-rich synthetic solution was prepared which contained 30 mg of Th, 0.463 mg of Fe, 0.100 mg of Ni and 0.2 mg of Cr(VI) per ml. Each of the two synthetic solutions was made 6 N with HCl and the iron from an aliquot of each of the solutions was extracted with hexone, after which the iron in the organic extract was determined flame photometrically. For samples concentrated with respect to thorium, the organic extract is washed with a 6 M HCl - 0.1 M HF solution prior to measurement of the radiant intensity of the iron. The test results are presented in Table I.

Discussion

From the test results as set forth in Table I, the limit of error in the determination of iron by this flame photometric method was found to be 10 per cent or less.

Part IV: Table I

Test Results for the Determination of Iron In Various Materials by Flame Photometry

(Iron extracted with hexone; hexone extract used for the flame photometric determination.)

NBS Standard Samples No.	Type	Iron Present, (x)	Iron Found, (y)	Limit of Error*	Bias**
		ppm	ppm	Per Cent	Per Cent
54b	Tin base	280	257	5	-8 ±3
63a	Copper base	5200	5200	5	0 ±3
157	Phosphor bronze	530	490	10	-8 ±4
Synthetic Solutions	mg/ml				
(1)	Th 30 Ni 0.1 Cr(VI) .2	463	463	4	0 ±2
(2)	U 10 Cu 0.5 Ni .05 Cr(VI) .1	16.2	15.9	7	-2 ±3

* Limit of error, L.E., 95 per cent probability level

** $\text{Bias} = \frac{(x - y)}{y} \pm \text{L.E.}/\ N$

References

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