The Halide Meter — The Myth and the Machine

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No evidence has been found to support the belief that the halide meter operates on the copper or copper-halide excitation principle. Rather, it is a more subtle mechanism, involving enhancement of the nitrogen band spectra in the presence of a halogen. The electrode material used serves only to conduct electric current. A stainless-steel and platinum electrode system along with an ultraviolet transmitting filter has been proposed which increases the sensitivity fourfold and the longevity of calibration by 50 to 100 times.

Introduction

THE SPARK-TYPE halide meter has been used for more than a generation to measure the concentration of halides and halogenated hydrocarbons in air. The meter has been used with good success to detect chlorinated hydrocarbons, but shows progressively less response to brominated, iodinated, and fluorinated materials. The ability of the halide meter to respond to any halogen has always been based on the theory of halogen interaction with a copper electrode and subsequent copper excitation in a spark source.[1] However, in spectral studies which have been undertaken, the evidence collected does not support this theory.

Experiments were conducted to ascertain the emission spectrum of the halide meter spark in the visible and ultraviolet regions. Several interesting and quite unexpected phenomena were observed: (1) No detectable copper lines or copper halide bands were noted at relatively high halogen concentrations of 2000 ppm; (2) halide meter readings could be obtained with a number of other metallic electrodes which contained no detectable copper; and (3) the same basic spectrum was always observed, no matter what electrode material was used or what halogen was sampled. Only the intensity of the bands changed when halogens were sampled.

The purpose of this study was to identify the spectrum produced, and to propose a more appropriate mechanism responsible for halide meter operation. A better understanding of the operational parameters has led to several changes in the electrode and optical filter system. These alterations have made possible large increases in sensitivity, stability, and longevity of calibration.

Experimental Procedure

The spark spectrum produced in air and in air-halogen mixtures was measured and recorded graphically by the apparatus shown in Figure 1. The shutter and green filter were removed from the halide meter and replaced with a quartz window. Light from the spark chamber passed through the window into a 0.25-meter Jarrell-Ash Ebert monochromator (82 to 410 A). The monochromator grating angle was changed with a dc timing motor powered by a 30-volt variable power supply. The motor was also attached to a variable potentiometer (voltage divider) which could alter the voltage from a 6-volt battery as it rotated. This voltage change was the signal to the x-axis (wavelength) on an x-y recorder.

Monochromatic light, exiting from the monochromator, was detected by an EMI-9536S

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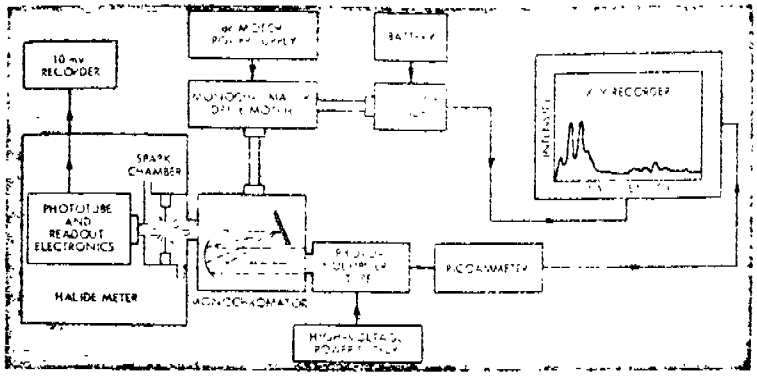

FIGURE 1. Block diagram of equipment used to obtain halide meter spectral data.

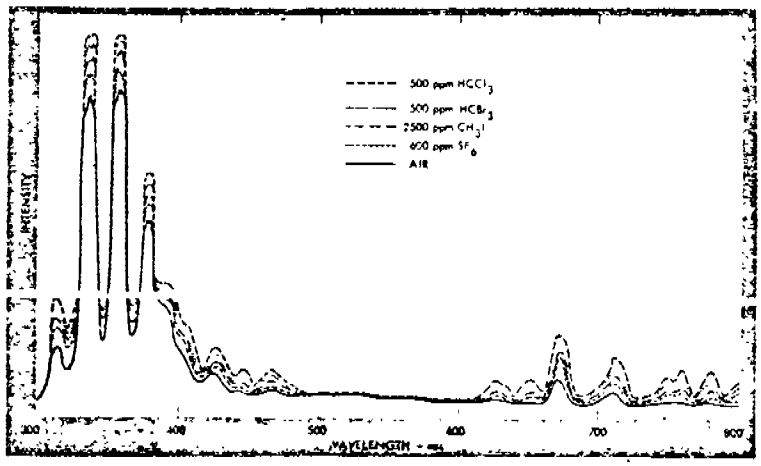

FIGURE 2. Spectra generated by halide meter spark in the presence of $HCCl_3$, $HCBr_3$, CH_3I, SF_6, and air.

photomultiplier tube powered by a John Fluke 412A high-voltage dc power supply. The signal from the phototube (intensity) was amplified by a Keithley 410 micromicroammeter and sent to the *y*-axis of a Varian F-80A *x-y* recorder. With this technique, light intensity versus wavelength (300 to 800 mμ) could be plotted simultaneously on the recorder.

A more precise spectral identification of the spectra was performed with a 3.4-meter Jarrell-Ash emission spectrograph. The halide meter was used as a source excitation unit. Light from the spark chamber was collected on photographic plates after a 30-minute exposure time. An iron pin was ignited with the regular Jarrell-Ash source unit. Since the iron emission lines are well known and accurately tabulated, accurate positions of the experimental lines or bands could be found. The dispersion of this system, 5 Å/mm, yielded accurate bandhead positions to ±1 Å.

Spark Spectra Produced from Halide Meter

Spectra were obtained from the halide meter spark source by using the usual platinum and copper electrode couple. Various halogenated and nonhalogenated hydrocar-

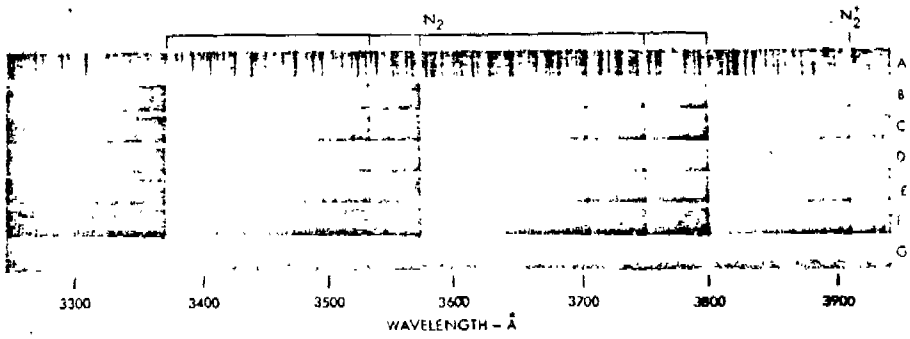

FIGURE 3. Photograph of halide meter spark spectra with various electrodes in air and air–Freon 12 mixtures. Line *A* is the reference iron pin. Lines *B* and *C* are the spectra from platinum and copper electrodes in air and 1000 ppm Freon, respectively. Lines *D* and *E* are the spectra from platinum and stainless-steel electrodes in air and 1000 ppm Freon 12. Lines *F* and *G* are the spectra from two platinum electrodes in pure nitrogen and oxygen, respectively.

bons were sampled. Figure 2 shows the spectra obtained when air, 500 ppm $HCCl_3$, 500 ppm $HCBr_3$, 600 ppm SF_6, and 2500 ppm CH_3I were sampled by the halide meter. Note that no new spectra have arisen, even though the halogen species sampled had changed. The only process observed was the intensification or enhancement of the air spectra. Other materials were sampled in concentrations up to 2000 ppm (NO_2, NH_3, NO, Hg, SO_2, acetone, benzene, and propane) but only SO_2 yielded a slight increase in spectral intensity.

A number of other electrodes were substituted for the platinum and copper combination, and several of these are shown in Tables I and II. All the electrodes used yielded the same basic spectra in approximately the same intensity as did the platinum and copper electrodes shown in Figure 2.

Identification of Spark Spectra

With the halide meter used as a source unit (except for the iron reference pin), accurate spectral photographs were taken with the 3.4-meter spectrograph. Air, air–gas mixtures, nitrogen, and oxygen were photographed; a typical segment of the results is shown in Figure 3. The top line (*A*) is the reference emission spectrum from the iron pin. Lines *B* and *C* are the spectra for air and 1000 ppm Freon 12, respectively, using a platinum and copper electrode couple. Lines *D* and *E* are the respective spectra from air and 1000 ppm Freon 12, using platinum and stainless-steel electrodes. Spectra from pure nitrogen and pure oxygen are shown in lines *F* and *G*. Note that: (1) No new spectrum appears even with the introduction of relatively large amounts of Freon 12; (2) the same spectra are produced from the copper and stainless-steel electrodes; (3) only band spectra are in evidence, indicating that the observed phenomena are primarily molecular rather than atomic; (4) all observed bandheads were classified as arising from excited nitrogen or N_2^+ molecules[2] and correspond in position to those lines produced from pure nitrogen in line *F*; and (5) oxygen does not contribute significantly to the overall spectrum.

Some copper (3247 Å and 3274 Å) and platinum (2659 Å, 2702 Å, and 2706 Å) lines were observed, but they were outside the spectral range of the photodetector. Other photographs were taken using both gold and platinum electrodes, but again the only spectra identified were those arising from nitrogen or ionized molecular nitrogen. The presence of halogen only increased the intensity of the spectrum.

Mechanism of Halide Meter Operation

From the spectrographic data obtained, one must suggest a mechanism vastly different from the copper atom or copper halide molecule excitation theory. No evidence has been seen to indicate that there is sufficient excitation of the copper or copper halide to

produce enough radiation to be detected. True, copper lines are easily visible on emission spectrograph photographic plates. However, under the low-amperage conditions of the halide meter (18 mA), copper excitation is not the major process. It can also be remembered that copper halides, especially CuCl, are readily observable in flames (Beilstein test). However, spark spectra are often vastly different from flame emission spectra, and CuCl has been observed in a spark only under specialized conditions of high vacuum in discharge tubes.[3] CuF and CuBr have never been observed by any means over the spectral region in which the meter operates.[3]

The dominant halide meter process present is ionization and excitation of the nitrogen molecules. It is the nitrogen spectrum upon which the meter is zeroed for background reading, and it is intensification of the nitrogen spectrum by the halide which causes the meter to respond. The exact role the halide plays, however, is mysterious and incompletely understood.

One series of experiments has indicated that the halogen might directly interact with the nitrogen molecule. Pure nitrogen gas was used to zero the instrument instead of air, and when 100 ppm chlorine gas in nitrogen was sampled, the meter responded in the characteristic manner. This would indicate that water, oxygen, carbon or its oxides, and other trace elements normally present were not needed as intermediates in whatever energy transfer process might exist. From this it would seem possible that the halogen acquired additional energy from the energetic electrons passing through the air space between the electrodes. This energy was then passed on to the nitrogen molecule through collisional processes, and finally was lost as radiation. This radiation was the increased nitrogen spectrum observed by the phototube of the halide meter.

There are other alternative explanations, but most of them are also lacking in supporting experimental evidence. Many theories, in fact, predict that quite the opposite phenomenon will be observed; that is, the nitrogen spectrum will be depressed rather than increased in the presence of a halogen. For example, it is well known that in a gas mixture, the gas with the lowest ionization potential will ionize and exite the easiest. However, in the mixture of nitrogen (15.5 volts), oxygen (12.5 volts), and chlorine (13.2 volts), the amount of nitrogen ionization and excitation increases as the chlorine concentration increases. This is just the opposite of what is predicted by the ionization potential data.

TABLE I
Effect of Electrode Material on Halide Meter Response to 100 Ppm Freon 12

Electrode		Response		
Upper	Lower	Signal (S)[a]	Noise (S)[b]	S/N
Platinum	Copper	35	3	12
Copper	Copper	45	4	11
Platinum	Stainless steel	35	2	18
Stainless Steel	Stainless steel	37	5	7
Platinum	Tungsten[c]	35	2.5	14
Tungsten[d]	Tungsten	30	5	6
Platinum	Brass	35	1.5	23
Brass	Brass	44	9	5
Platinum	Platinum	33	2	17
Gold	Gold	34	2	17
Platinum	Aluminum[e]	28	4	7
Platinum	Carbon	30	6	5
Platinum	Tantalum[f]	—	—	—
Platinum	Molybdenum	7	7	1
Platinum	Iron	57	4	14

[a]Reading on meter when 100 ppm Freon 12 was sampled.
[b]Background fluctuations when air only was sampled.
[c]Yellow powder (WO_3 or WO_2Cl_2) formed on tungsten electrode
[d]Upper electrode ignited and burned after about 5 minutes of sampling
[e]Aluminum electrode ignited and burned after 14 minutes of sampling.
[f]Tantalum electrode ignited immediately upon spark activation.

Effect of Electrode Material

Twenty-one pairs of electrodes were substituted in the halide meter. The response to 100 ppm Freon 12, the background noise, and the ratio of these two values are tabulated in Table I for fifteen pairs of electrodes. Note that all the electrodes, except those which ignited at the high spark temperatures (1100°K), gave a meter reading. It can also be seen that the best signal-to-noise ratios were achieved when a relatively inert material (platinum or gold) was used as an upper electrode. Platinum and gold greatly decrease the amount of oxide formation, which causes

TABLE II
Effect of Various Filters on Halide Meter Response to 100 Ppm Freon 12[a]

Electrodes		Filter														
		UG-5[b]			4-76[c]			7-60[d]			5-60[e]			H. M. F.[f]		
Upper	Lower	S[g]	N	S/N	S	N	S/N	S	N	S/N	S	N	S/N	S	N	S/N
Platinum	Stainless steel	70	1.5	47	15	0.5	30	37	1.0	37	20	0.5	40	47	2.5	19
Platinum	Alumel	59	1.5	39	14	0.5	28	32	1.5	21	14	0.5	28	40	1.5	27
Nickel	Nickel	59	2.0	30	17	1.0	17	34	1.5	23	12	0.5	24	40	1.5	27
Platinum	Gold	59	2.5	24	23	3	8	36	2	18	17	1	17	41	1.5	27
Platinum	Platinum	70	3.5	20	15	0.5	30	43	2.5	17	20	0.5	40	56	2.5	22
Platinum	Copper	75	10	7.5	12	2	6	44	2	22	21	3	7	51	4.0	13

[a] Readings generated by an RCA phototube exhibiting S4 type spectral response.

[b] Schott & Gen filter, 2.3 mm, maximum transmission at 325 mμ (90%) and 725 mμ (50%) with less than 0.1% transmission from 425 to 680 mμ. Spectral characteristics similar to Corning filter No. 7-54.

[c] Corning filter, 5.0 mm, maximum transmission at 480 mμ (80%), effective band width 375 to 575 mμ.

[d] Corning filter, 4.6 mm, maximum transmission at 350 mμ (70%), effective band width 325 to 380. A smaller band also appears with a maximum transmission at 740 mμ (10%) and an effective band width from 720 to 750 mμ.

[e] Corning filter, 4.7 mm, maximum transmission at 420 (65%), effective band width from 380 to 470 mμ.

[f] Halide meter filter supplied with the instrument, 3.0 mm, maximum transmission at 420 (70%), effective band width from 380 to 460 mμ.

[g] S—signal from 100 ppm Freon 12; N—background noise with no Freon 12 being sampled, S/N—signal-to-noise ratio.

poor electrical conduction and high background noise levels.

The copper electrode used in the halide meter is a rather poor choice. Under the extreme conditions of electrical discharge, the halogens are present in a highly reactive state. They attack the copper electrode and form a copper halide which coats the filter, slits, and electrodes. This changes the gap distance, which disrupts the longevity and accuracy of the calibration curves.

Comparative weight loss data for copper and stainless-steel electrodes were studied when 0.5% Freon 12 was sampled for 30 minutes. The copper electrode lost 6.3 mg and 0.9 mm of length, while a stainless-steel electrode lost only 0.08 mg with no discernible reduction in length. This would indicate a life of up to 50 to 100 times as long as that of the copper electrode.

Effect of Various Filters

Maximum sensitivity could be improved if those regions which showed the greatest enhancement could be better optically isolated from those areas in which few or no bands were present. The ultraviolet region (300 to 425 mμ) seemed to be one of the more promising areas to study. Four filters were tried in an attempt to improve the sensitivity. Filters were substituted for the one supplied in the commercial instrument; the comparative results are shown in Table II. Meter response (signal) to 100 ppm Freon 12 and background (noise) were measured, and the signal-to-noise ratio was calculated for various electrode pairs. The UG-5 filter, in general, gave not only the best signal but the best signal-to-noise ratio as well.

Effect of Both Filter and Electrode Material

Table II also shows the effect of both electrode and filter on meter response. The best combination is the platinum upper and stainless-steel (soft-tempered, 0.051-inch diameter) lower electrodes with a Schott and Gen UG-5 (or Corning 7-54) filter. Typical response curves are shown in Figures 4 and 5. Figure 4 is the response to 100 ppm Freon 12. Note that the background noise level is three times as high and the signal is about 30% lower when the platinum and copper electrodes are used with the regular filter.

Figure 5 shows an even more striking comparison when methyl iodide is sampled while the platinum and copper electrodes are used.

	H. M		F [a]
S/N	S	N	S/N
40	47	2 5	19
28	40	1 5	27
24	40	1.5	27
17	41	1.5	27
40	56	2 5	22
7	51	4 0	13

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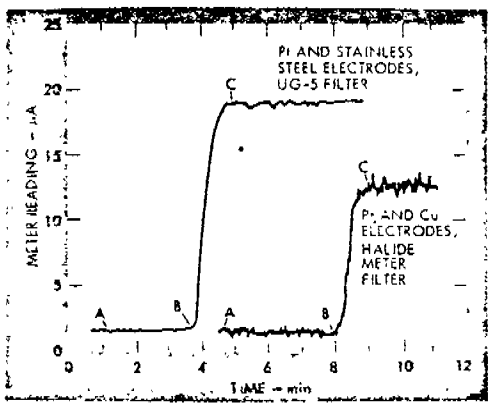

FIGURE 4. Halide meter response curve to 100 ppm Freon 12. Air background is measured from time *A* to *B*. The Freon 12–air mixture is sampled at *B* and reaches maximum scale reading at time *C*. Note greater response and lower background noise when the stainless-steel electrodes and UG-5 filter are used.

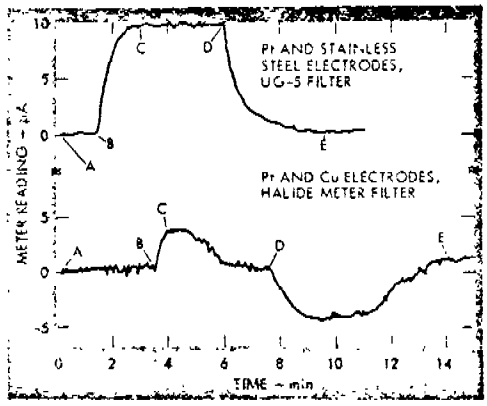

FIGURE 5. Halide meter response to 1000 ppm CH_3I. Background is observed from time *A* to *B*. CH_3I is sampled at *B* and reaches maximum meter reading at time *C*. At time *D* pure air is sampled, and the original background observation is reached at *E*. Note erratic and inconsistent results when the platinum and copper electrodes are used with the halide meter filter.

The meter reads about 4 μA when the contaminant is introduced, but gradually drops to zero even while the methyl iodide is being sampled. The meter drops below zero when fresh air is again sampled, but it returns to the approximate original base line several minutes later. Clearly this system was not useful even at a comparatively high concentration. The platinum and stainless-steel electrode–UG-5 filter system, however, proved to be extremely stable and demonstrated useful response characteristics.

Figure 6 gives an overall indication of the response gains when the stainless-steel elec-

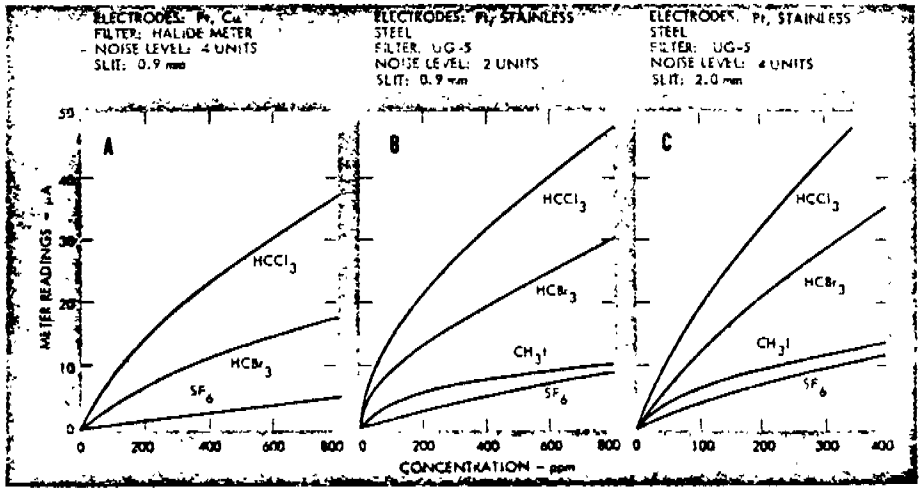

FIGURE 6. Halide meter calibration for halides using various conditions. Graph *A* was obtained under normal conditions. Graph *B* shows the gain in response and diminution of background when a stainless-steel electrode and UG-5 filter are used. Graph *C* shows the true sensitivity gain over the conditions in *A* because the noise levels have been equated.

trode and a UG-5 filter are used to detect the various halogens with the halide meter. Graph *A* shows a calibration curve under the standard instrument conditions. Graph *B* shows the increases in sensitivity obtained when a stainless steel electrode and UG-5 filter are used. The same electrode and filter conditions are used in obtaining graph *C*, except that the slits were opened to approximate the noise conditions encountered when the platinum and copper electrodes were used with the halide meter filter. This gives a truer indication of response gains when electrode and filter substitutions are made. Note that the new conditions increase the response fourfold for chloroform, bromoform, and sulfur hexafluoride. Methyl iodide was easily detected, whereas platinum and copper electrodes yielded erratic results.

Conclusions

No evidence has been found to support the belief that the halide meter operates on the copper or copper halide excitation principle. Rather, it is a more subtle mechanism involving an incompletely understood halide interaction with the nitrogen molecule. In the presence of the halide, the nitrogen spectrum becomes more intense, and the photodetector responds to this enhancement. The only important qualification of the electrode material is that it produce a smooth, stable spark and be reasonably resistant to halogen gases.

Experiments have shown that with a platinum and stainless-steel electrode couple and an ultraviolet filter system, a manyfold increase in sensitivity is often realized. Some solvents, such as methyl iodide, could not be clearly measured with a platinum and copper electrode couple. However, with stainless steel, as an electrode material, such materials are easily and accurately detected. Some nonhalogenated materials such as sulfur dioxide and other sulfur derivatives could be measured as well.

Stainless-steel electrodes have been found to increase the longevity of calibration by 50 to 100 times because of their resistance to spark decomposition products. These electrode and filter changes have made it possible to measure all halogens more accurately and thus greatly increase the general reliability of the instrument.

References

1. *Davis Halide Meter Instruction Manual*, Bulletin No. 1148 Davis Instrument Division, Newark, New Jersey
2. Pearse, R. W. B. and A. G. Gaydon *The Identification of Molecular Structure*, 3rd Ed., Chapman and Hall Ltd., London (1963)
3. Rao, P. R., and J. K. Brody: *J. Chem. Phys. 35:* 776 (1961)

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Dictionary of Mining and Mineral Industry Terms

A comprehensive dictionary of mineral science and technology, published by the Interior Department's Bureau of Mines, has been placed on sale by the Superintendent of Documents, U. S. Government Printing Office. Titled *A Dictionary of Mining, Mineral, and Related Terms*, the 1269-page volume contains approximately 150,000 definitions for some 55,000 separate entries. Included are scientific and engineering terms, words common to particular mineral-producing localities or regions, and abbreviations generally used in the technical literature on mineral technology published throughout the English-speaking countries of the world. Price of the new publication is $8.50.

Up-to-date definitions reflect changing usage of older terms as well as additions to the vocabulary, but some older definitions, considered to be of value in historical research, are also included. The authority or source for each definition is provided, giving an indication of the time and place in which the term was first used. The bulk of the entries relate to metal and coal mining, quarrying, geology, metallurgy, glassmaking, ceramics and clays, and minerals and rocks of economic significance.

A Dictionary of Mining, Mineral, and Related Terms was compiled and edited by Paul W. Thrush and the Staff of the Bureau of Mines. A copy of the dictionary can be purchased from the Superintendent of Documents, U. S. Government Printing Office, Washington, D.C. 20402. It is not sold by the Bureau of Mines.

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