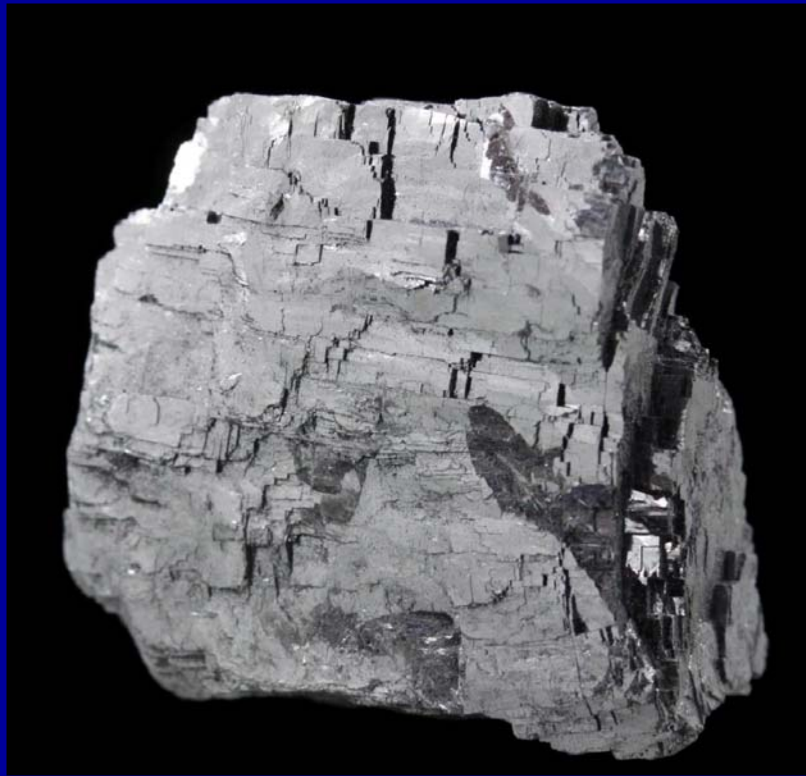


"it pays to be biased"

S1

S2 Title

S3 Structure

The following is some work I did for an MsC between 1970 and 1973, after some discussion with some people from CSIRO and National Standards re the problem of discrimination of sulphides and graphitic using IP. I noted the property main difference was that sulphides were semi conductors and clays/graphite were not.

The problem was, what was the best way to use these property differences.

Having built crystal sets in years gone by, I was familiar with the properties of Galena as a diode. The project was then directed at looking at the properties of semi conductors as well as investigating any previous work in this field.

The project was always focused on trying to develop a system that would work in the field under normal field conditions and current densities.

S4 Cats whisker and Galena

NON-LINEAR CONDUCTION IN SULPHIDES

(an old concept come of age?)

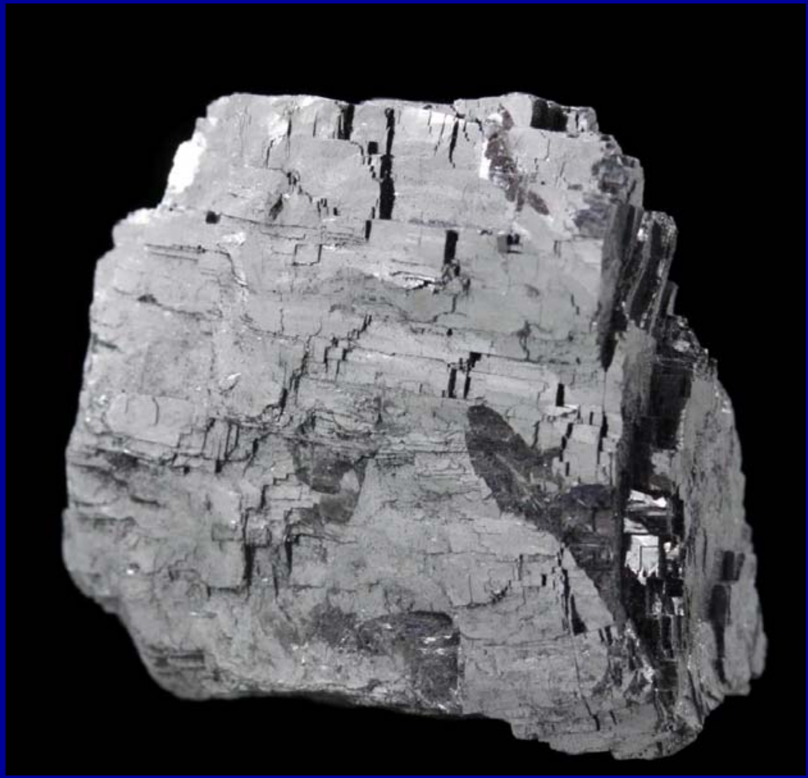
BOB WHITE

ASEG CONFRENCE PERTH 2015

NON-LINEAR CONDUCTION IN SULPHIDES

- **Early History 1901- 1945**
- **Early experiments 1968-1975**
- **Canadian follow-up 1980. Chinese 1995**
- **Future applications**

ASEG CONFRENCE PERTH 2015

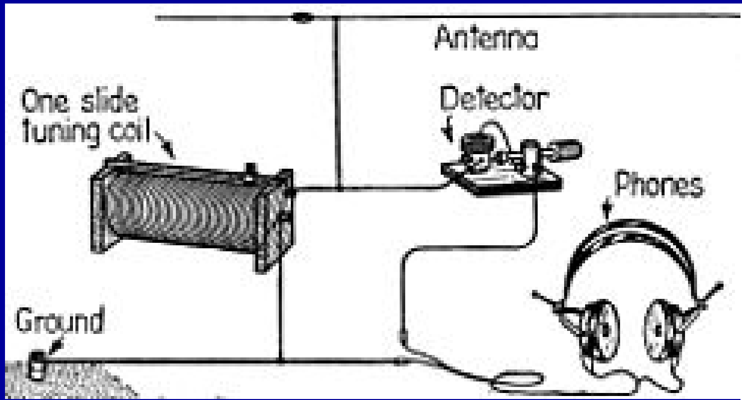


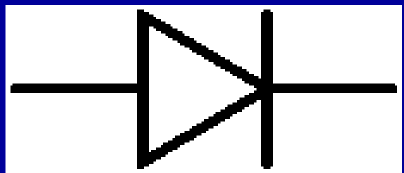
S5 Unlike modern radio stations that transmit sound, the radio transmitters during the first three decades of radio transmitted information by telegraphy; the operator turned the transmitter on and off with a switch called a telegraph key to spell out messages in Morse code, consisting of different length pulses of radio waves called "dots" and "dashes". So early radio receiving apparatus merely had to detect the presence or absence of the radio signal, not convert it into audio. The device that did this was called a detector.

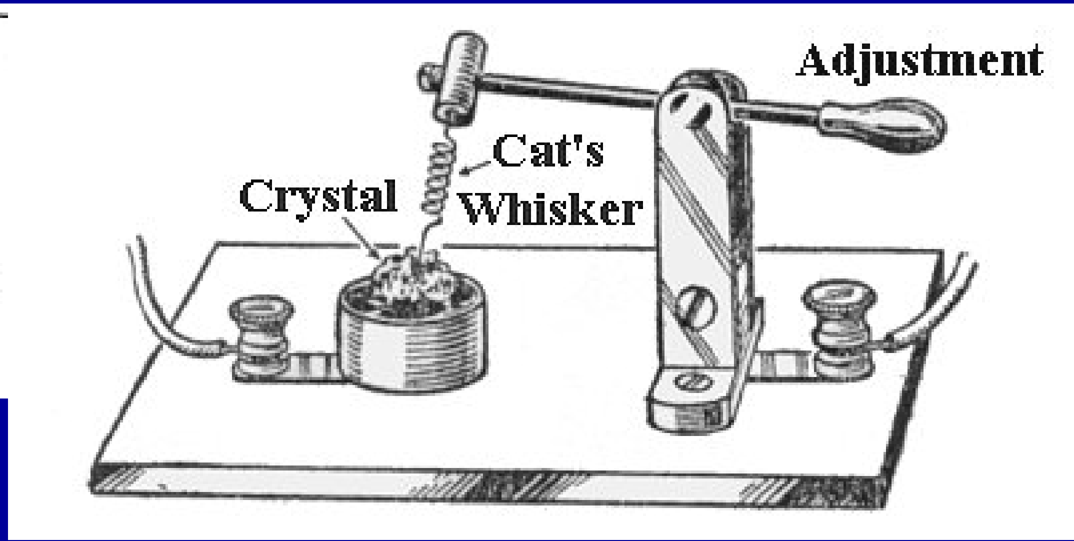
The crystal detector was the most successful of many detector devices that were used in the early days of radio. It replaced earlier electrolytic, magnetic, and particularly coherer detectors in radio receivers around 1906. Later, when AM radio transmission was developed to transmit sound, around World War I, crystal detectors proved able to receive this as well.

The "unilateral conduction" of crystals, as it was then called, was discovered by Braun, a German physicist, in 1874, before radio had been invented.

Indian scientist Bose was the first to use a crystal to detect radio waves, in his pioneering experiments with microwaves in 1894, applying for a patent on a galena detector in 1901







The modern circuit symbol for a diode originated as a schematic drawing of a cat's-whisker detector

The "unilateral conduction" of crystals, as it was then called, was discovered by Ferdinand Braun, a German physicist, in 1874 *at the University of Würzburg, before radio had been invented.[9] Indian scientist Jagadish Chandra Bose was the first to use a crystal to detect radio waves, in his pioneering experiments with microwaves in 1894, applying for a patent on a galena detector in 1901*

SEARCH FOR SULPHIDES

RESISTIVITY mapping can also respond to other conductors ie shales, clays and salt water.

IP mapping can also respond to shales, clays and fences.

PROBLEM. How to discriminate other chargeable sources from sulphides.

SEARCH FOR SULPHIDES

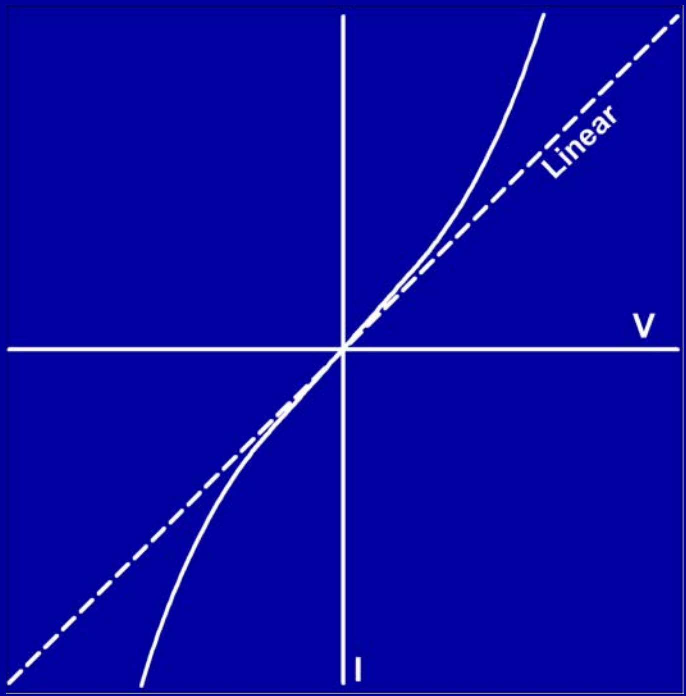
RESISTIVITY mapping can also respond to other conductors ie shales, clays and salt water.

IP mapping can also respond to shales, clays and fences.

PROBLEM. How to discriminate other chargeable sources from sulphides.

Sulphides are semi-conductors.

The conduction in most homogeneous materials is linear, that is the current-voltage graph is a straight line. This relationship holds also for semi-conducting materials. But in reality there is always some heterogeneity. In the more usual case of multi-mineral aggregates the inhomogeneity is quite complex. It is this inhomogeneity that causes non-linear conduction within semi-conductors.



There are a number of methods of exploiting this nonlinear conduction property as a possible exploration tool.

Slide 8 The first is simply to monitor the voltage increase as the current increases and plot these, studying the distortion in Lissajous figures.

Slide 9 White is with no non linearity, Green is with some non linearity, Yellow is with linear part removed.

Slide 10 The problem is the IP effect gets in the way. The polarisation can be seen in the Lissajous figures. At field current densities the polarisation swamps the non linear effect.

Slide 11 When currents of two different frequencies are passed through a linear network the resultant output will contain only those two frequencies. If a non-linear element is present somewhere in the network then the output contains the original two frequencies, harmonics of the two frequencies, and inter-modulation products of the two frequencies.

By studying these inter-modulation products it is possible to detect the non linear elements in a system, ie the sulphides.

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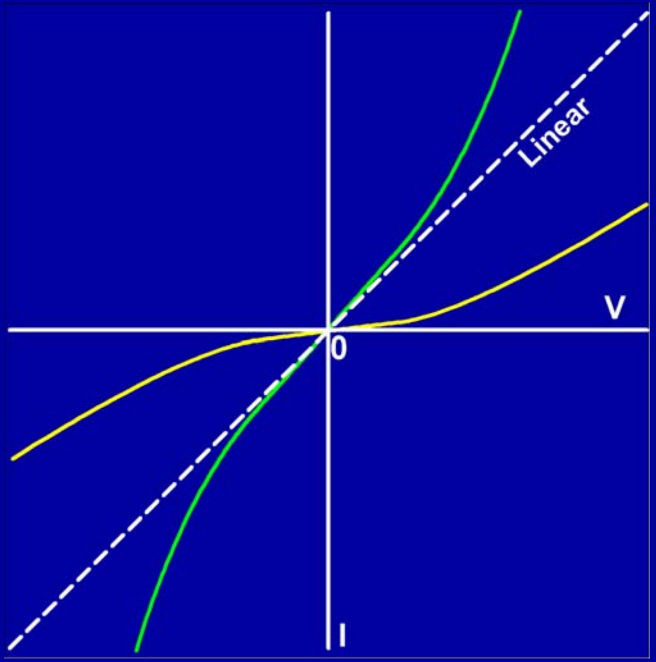

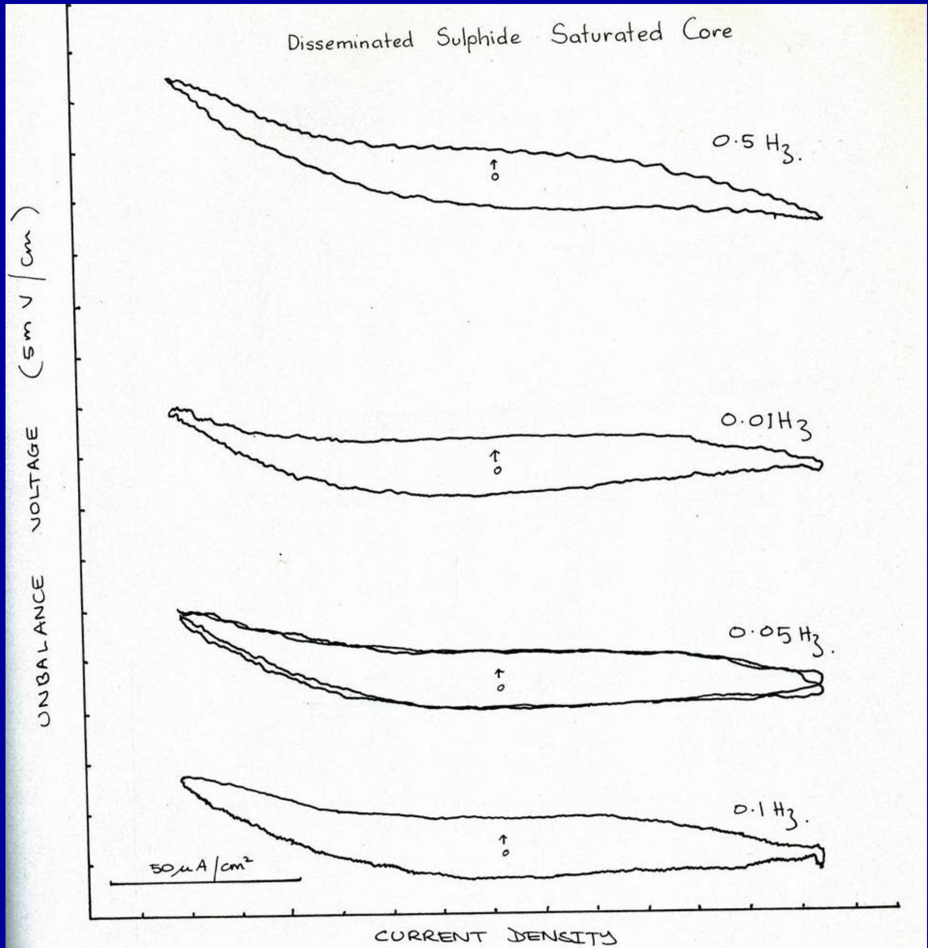

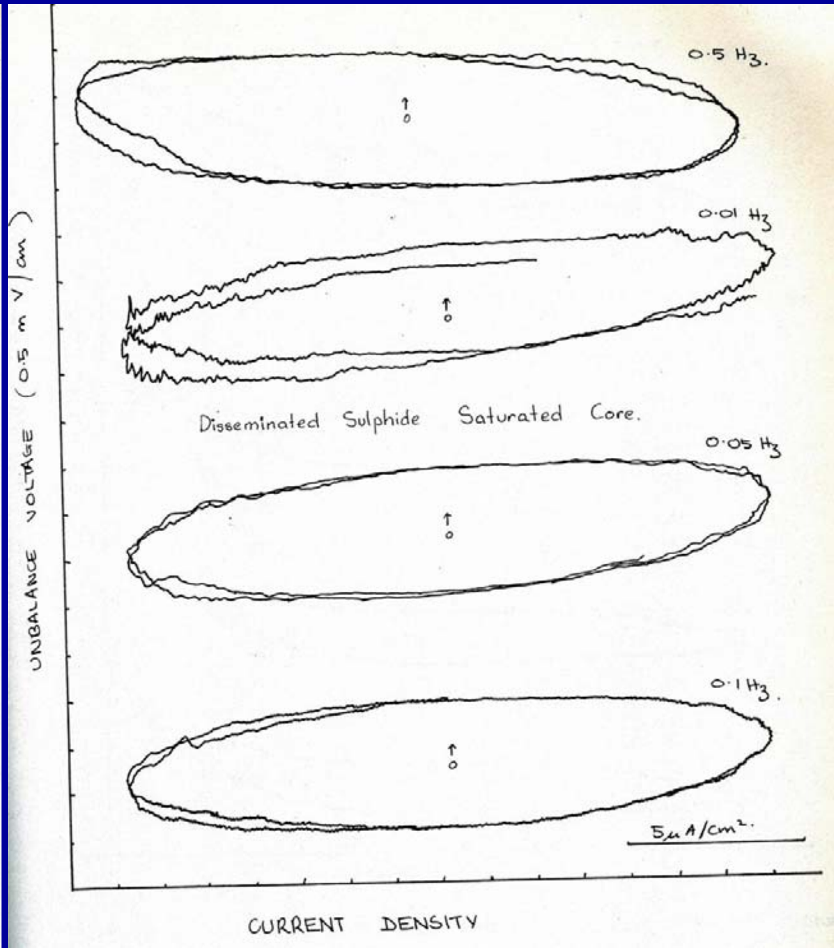

50uA/cm²

5uA/cm²

IP effect

Theoretically it is possible to use one frequency and look at any harmonics developed, but this presumes that the signal generator and associated electronics do not contain or produce any harmonics of the fundamental.

The use of 2 frequencies and the study of inter-modulation products, ie w1-w2, w1+w2 or w2-w1, w2+1 gets around this problem provided that the sum and difference frequencies are not the same as the harmonics of the 2 fundamental frequencies.

Similarly pick the frequencies so that the inter-modulation products are not harmonics of the mains.

When currents of two different frequencies are passed through a linear network the resultant output will contain only those two frequencies. If a non-linear element is present somewhere in the network then the output contains the original two frequencies, harmonics of the two frequencies, and inter-modulation products of the two frequencies.

Slide 12 Published work on nonlinear conduction in minerals is limited to two main sources, one Russian and one Canadian.

The Russian work was mainly produced by Y.B.Shaub and is reported in a series of papers published in the Bulletin of the Academy of Sciences, Earth Physics. His first in 1965 discussed some of the theoretical aspects of nonlinear conduction in rocks, as a tool for electrical prospecting. The use of a two frequency method was discussed, along with possible methods of analysis. He proposed five types of nonlinear conduction:

a. proportional to current strength.
b. proportional to the modulus of current strength.
c. proportional to the square of current strength.
d. proportional to the cube of current strength .
e. dependent not on the strength but only on the direction of the current.

He also stated that "these effects, or at least some of them, decrease as frequency rises". Shaub, in most of his work, made no reference to the origins of the non-linear effects

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No reference to the origins of the non-linear effects

Slide 13 Research done by the Canadian Geological Survey into non-linear electrical phenomena was reported in a paper by Katsube, Ahrens and Collett (1973). In their work they use what is basically a single frequency method, studying the distortion in Lissajous figures caused by non-linear conduction.

In this paper they suggested that electrical nonlinear phenomena occur above a certain charge density. This critical charge density is dependent on frequency in such a way that the charge density necessary to achieve nonlinearity decreases with decreasing frequency.. They also tested a galena sample and concluded that the effects took place at the electrolyte-mineral interface. They also suggested that charge densities necessary to achieve nonlinear conduction could only be achieved in bore holes.

Slide 14.

Katsube, Ahrens and Collett (1973).

Single frequency method, studying the distortion in Lissajous figures caused by non-linear conduction.

They suggested that:-

<u>Electrical non-linear phenomena occur above a certain charge density</u>.

<u>This critical charge density is dependent on frequency</u>.

They also suggested that charge densities necessary to achieve non-linear conduction could only be achieved in bore holes.

All previous studies indicated that the non-linear effects were so small to be non detectable under field conditions.

They may be detectable in bore hole surveys if the current density is large enough.

What causes non-linear conduction?

Slide 15 The conduction in most homogeneous materials is linear, that is the current-voltage graph is a straight line. This relationship holds also for semi-conducting materials. But in reality there is always some heterogeneity. In the more usual case of multi--mineral aggregates the inhomogeneity is quite complex. It is this inhomogeneity that causes non-linear conduction within semi-conductors.

It is generally the point contact/junctions between 2 “dissimilar” semiconductors.

We won’t go into transistor theory hear except to say a knowledge of how the various junctions behave helps to understand some of the concepts mentioned later.

The study concentrated on the 2 frequency method where 2 frequencies were injected into the sample and a series of intermodulation products measured.

What causes non-linear conduction?

The conduction in most homogeneous materials is linear, that is the current-voltage graph is a straight line. This relationship holds also for semi-conducting materials. But in reality there is always some heterogeneity. In the more usual case of multi--mineral aggregates the inhomogeneity is quite complex. It is this inhomogeneity that causes non-linear conduction within semi-conductors.

It is generally the point contact/junctions between 2 "dissimilar" semiconductors.

Slide 16 Why did I not stop my studies at this point???

1. I felt that the non-linearity was not caused by the electrolyte mineral interface but arose at the semiconductor interface or junction.
2. If this was true then adding a DC bias, as is done with transistors, could push the non-linearity up to a point where it could be observed under field conditions.

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Slide 17 The frequencies used in this work were 70 Hz and 56 Hz. These were chosen on a number of criteria. The first was to keep the frequencies low, as any future field work would have to be done at low frequencies; also an early Russian paper (Shaub et al. 1971) noted that the non-linear effect seemed to diminish with increasing frequency. The frequencies were chosen so that the primary harmonics of the frequencies used did not lie on or near the expected intermodulation products or mains harmonics.

$\omega_l + \omega_2$ 126* frequency studied

	Frequency Hz
Mains	50
ω_l	56
ω_2	70
$2\omega_l$	112
$\omega_l + \omega_2$	126* frequency measured
$2\omega_2$	140
mains	150
$2\omega_l + \omega_2$	182
$2\omega_{2} + \omega_l$	196

In 1970 electronics was not like today. Off the shelf equipment was not up to the job ie not linear enough. All front end amps had to be designed and carefully hand built with matching components. A modern (1972) HP spectrum analyzer was not linear enough.

Slide 18 As ancient (1958) **valve** wave analyser (General Radio model 736A) was used to measure the intermodulation frequency being the only instrument at the time that was linear enough.

Slide 19 Sandstone was one of the first samples tested since it should produce no intermodulation products. The conduction through sandstone should be only through its saturating electrolyte and not through the host mineral which is far more resistive. Sandstone produced no detectable I.M. products with current densities up to several milliamps/cm^2, even with a D.C. bias. Repeated measurements of the sandstone sample were used to keep check of the equipment during the remainder of the testing.

Several samples of rock from Captains Flat containing from 5% to 60% sulphide were tested using no D.C. bias. Only in the hundreds of $\mu A/cm^2$ range was there any sign of non-linearity present. This was still well within the noise region of measurement and no positive results could be obtained.

Wave Analyser (General Radio model 736A)

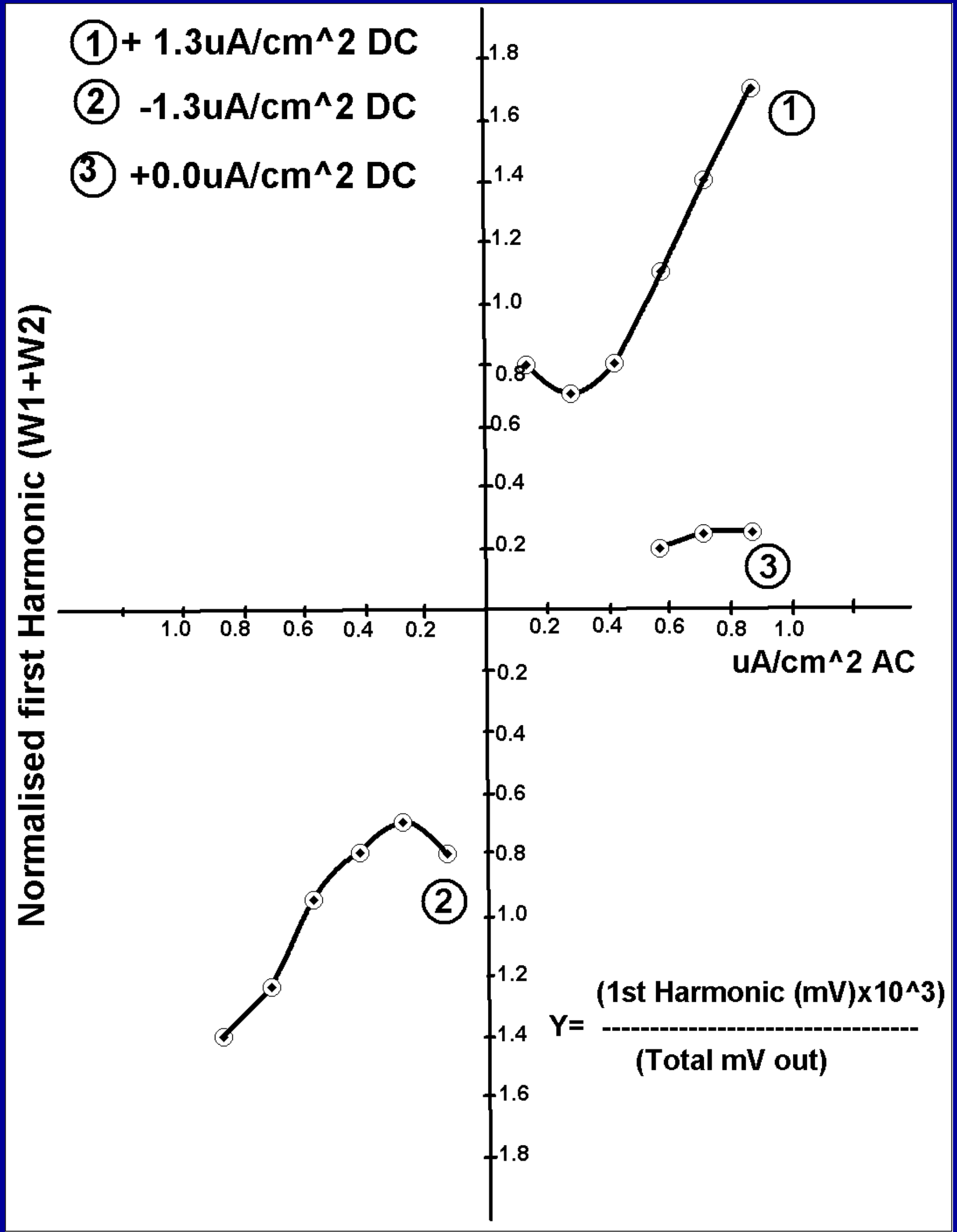
Sandstone used as a check on the system linearity.

The best frequency for study was found to be 126 Hz because it appeared to be the largest of the I.M. products. It is also sufficiently separated from the 70 Hz carrier for interference to be negligible.

The results using a D.C. bias were much more encouraging. **Slide. 20** shows the results using a disseminated sulphide from Captains Flat. This rock contained about 10% sulphide conentrated in blebs of the order of 1mm across. The graph is a plot using constant D.C. bias while varying the A.C. signal input. The A.C. current density is plotted against the ratio of the voltage output at 126 Hz (ω 1 + ω 2) and the total voltage out, multiplied x 10^3, i.e.

Slide 20 shows the plot of zero D.C. bias and 1.3μA/cm^2 bias using both positive and negative biasing. There is a marked increase in the intermodulation product (I.M.) with an increase in D.C. bias current. The turnover of the graphs at 0.26μA/cm^2 is because the I.M. product has dropped into the noise level region and the total output voltage continues to get smaller while the I.M. reading remains the same.

Analysing these results we note a number of things. The first is an increase in the non-linearity with an increase in direct current bias. This increase in non-linearity is quite marked, a doubling in bias current more than doubling the non-linear output plotted.



DC bias v No DC Bias

Curves 1 & 2 have DC Bias.

Curve 3 has no bias

Role over of curve at low current is because IM product has dropped to a constant noise and input voltage continues to drop.

Slide. 21 is the same rock but at higher current densities. The D.C. currents are ± $1.3\mu A/cm^2$ and ± $2.6\mu A/cm^2$.

The negative D.C. biased cores do not give the same results as the positively biased ones. This non-reversibility of the curves was noted to varying degrees in all of the tests done.

Slide. 22. This has many of the same features as the previous curves with the curve for negative D.C. bias being different from the positive curve. Note that this curve is D.C. current density plotted against mV of the intermodulation product ($\omega 1 + \omega 2$) since the total voltage out remains the same. The A.C. current density in this case is 3.2μA/cm2.

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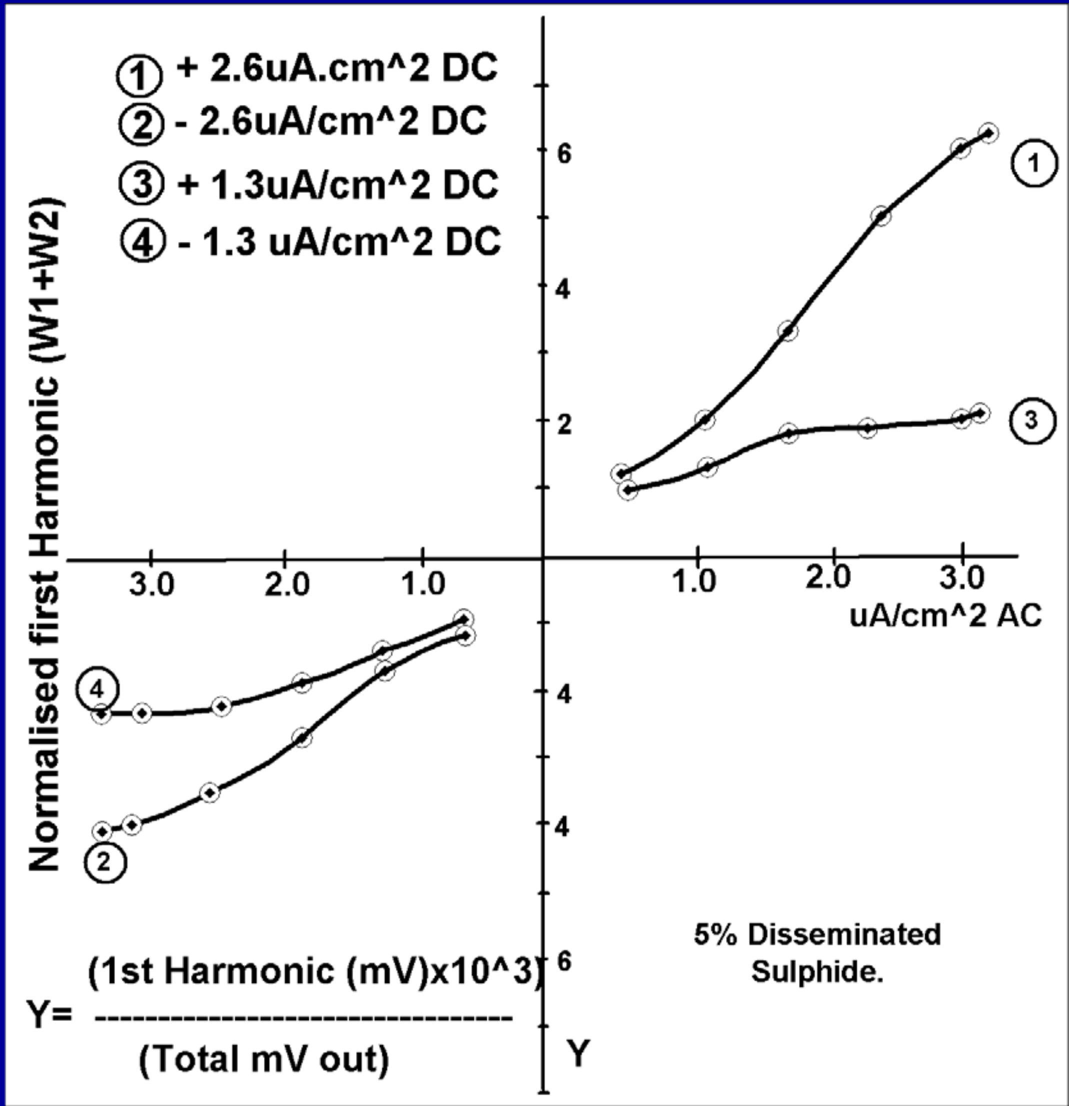
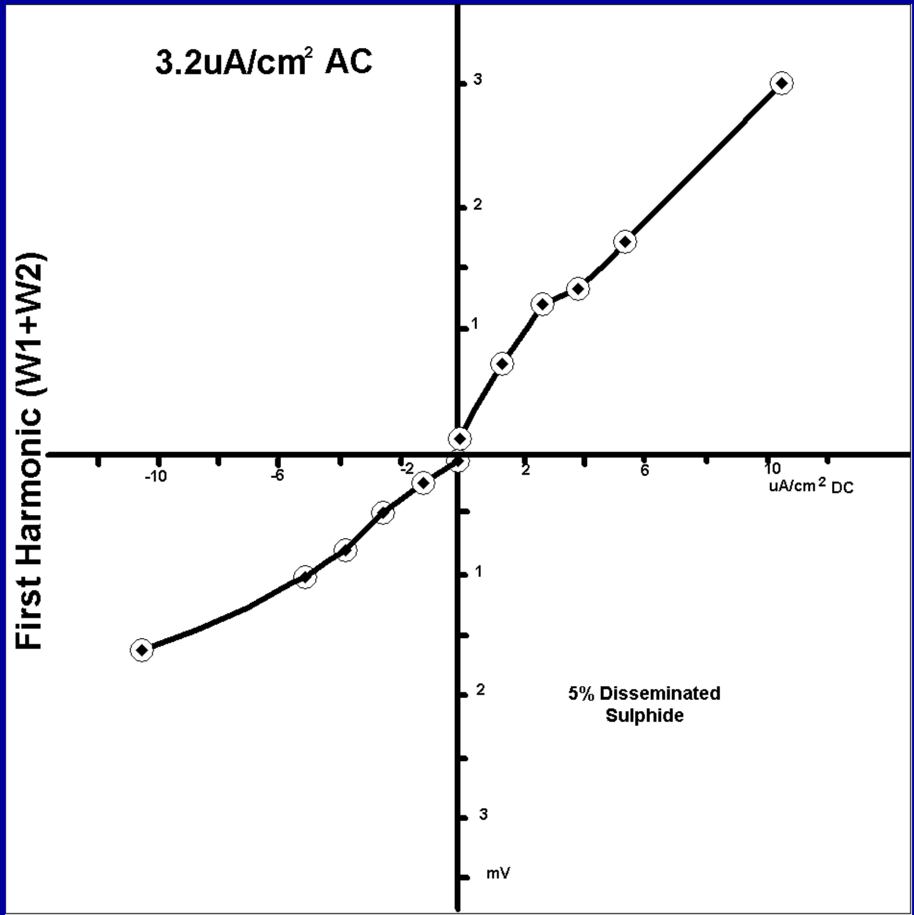


Higher current densities

2 different DC current densities



Constant AC and Varying DC bias

Where to from hear (circa 1973)

Slide 23 Where to from hear (circa 1973)

Slide 24 As noted in the study, the application of a DC bias increased the “mixing” some 3 or 4 fold. The intermodulation product was still some 60dB down on the primary signal.

To help signal processing it should be possible to “modulate” the DC bias using a square wave of say 8seconds on and 8 seconds off. Subtracting the “off” readings from the “on” readings may help enhance the signal.

For test work a 24 bit A to D (<$1000) with a suitable front end amplifier for a receiver should give suitable resolution and dynamic range. The transmitters could be 2 high powered audio amplifiers with suitable sign wave generators driving them.

Where to from hear (circa 1973)

Application of a DC bias increased the “mixing” some three or four fold.

The intermodulation product 60dB down on the primary signal.

“Modulate” the DC bias using a square wave of say 8 seconds on and 8 seconds off. Subtracting the “off” readings from the “on” readings may help enhance the signal. If the method proved viable the DC modulation could revert to the typical IP frequency of 2 seconds on and 2 seconds off and the method could be run as part of a normal IP survey.

Where to from hear (circa 1973)

Electronics has come a long way in 40 years, especially digital.

Receivers:-24 bit A to D with a suitable front end amplifier and filter for a receiver would give suitable resolution and dynamic range.

Transmitters:- 2 high powered audio amplifiers with suitable sign wave generators driving them.

Future developments

Slide 26 A more detailed study of the non-linear effects and a better understanding of exactly how and where they occur in mineral the assemblages. This may lead to better ways to measure and use them.

An obvious next step would be to revisit the down hole survey techniques using new arrays and processing.

The development and integration of IP/Resistivity surveys.

The development of inversion techniques for these data sets in conjunction with resistivity and IP information.

Development of airbourne systems? Large gradient surveys with drones.

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A copy of the 1974 MSc thesis can be found at the website below, along with some references to more recent work by other authors.

http://www.tooronga.com/nonlin/

Later References.

http://csegjournal.com/assets/pdfs/archives/1980_12/1980_Mitchell_G_electrical_prospecting.pdf

ELECTRICAL NON-LINEAR PARAMETERS OF ROCKS

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October 1974 M. St-Amant

Available on Tooronga web site.

Later References.

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NONLINEAR EFFECT OF THE DUAL-FREQUENCY IP SPECTRUM[①]

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