THERMOCOUPLES FOR INFRARED SPECTROMETRY

by

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INTRODUCTION

Recently Van Zandt Williams (13) presented a complete review on infrared instrumentation and techniques. As he pointed out in his article, the greatest fundamental handicap the infrared spectroscopist faces is the low sensitivity of the available energy detectors. Many types of heat detectors have been tried, but methods of improving infrared detectors still represent the largest single instrumental research effort in the field today.

In tracing back the historical development of detectors, it is very difficult to find a dependable relative valuation of the different types. Infrared radiation was discovered by William Herschel (7, p.5) in 1800 when observing the temperature rise of thermometers placed in different positions in the sun's spectrum. In 1840 the son of the discoverer (7, p.33) introduced a new method of detection. In his experiment, a sheet of soot blackened and alcohol moistened paper was set under the sun's spectrum. It was noticed that dried spots formed in the infrared region first. As the rate of the evaporation of alcohol depends directly on the heat energy of the absorbed radiation, the photographed pattern thus provided a recorded infrared spectrum. In 1880 the bolometer, the first really sensitive infrared detector, was invented by Langley (8). In an attempt to get away from the vibrations and drift of galvanometers due to extraneous electrical and magnetic disturbances, the radiomicrometer and the radiometer were introduced. Coblentz (2, p. 152-176) who made a thorough study of instruments for measuring radiation, considered the radiometer to be very sensitive and stable, but its period for these conditions was of the order of a minute.

From 1910 to 1935, these various types of heat detectors gradually gave way to the combination of thermocouple and galvanometer, which in turn developed into the almost universal detector-amplifier combination now in preferred use. Johansen (6) in 1910 gave an excellent theoretical treatment of thermopile sensitivity and the period 1930-1934 saw this treatment carried further.

Although, up to 1925, the standard method for measuring infrared spectra was manual setting of the spectrometer at the desired frequency and visual observation of galvanometer deflections representing sample in and sample out energies, as early as 1907 automatic photographic infrared recording was used by W. Weniger (12). In his apparatus, the prism was rotated automatically while the galvanometer spot of light fell on a continuously moving photographic plate so as to give a continuous spectral reading. In this way a great saving in time was accomplished.

The major difficulty encountered in such continuous recording was the zero drift of the galvanometer and the detector caused by ambient temperature changes. This was somewhat minimized through the use of compensating junctions, but such junctions take an appreciable time to indicate changes in received radiation.

To overcome galvanometer drift heat detectors have been made fast enough to respond to a chopped radiation beam of 5 to 15 c.p.s.. The a.c. signal permits the use of a transformer so that electronic amplification may be used to replace the ultra sensitive Thompson four-coil galvanometer.

Such investigation supplemented by military research for signaling and detecting purposes, have now furnished good, fast, stable detecting and recording systems of many types, although there has been no appreciable gain in ultimate sensitivity over those available in the 1930's.

THEORETICAL TREATMENT OF THE OPTIMUM DESIGN

Johansen in his article published in 1910 (6) pointed out that: (i) the galvanometer resistance should be equal to the resistance of the thermoelements; (ii) the radii of the two wires of the thermoelement should be so chosen that the ratio between the heat conductivity and the electrical resistance is the same in both; (iii) the heat loss through radiation from the junction should equal the heat loss by conduction; and (iv) the radiation sensitivity should be proportional to the square root of the exposed surface.

Since that time, the design of thermopile-galvanometer systems for maximum deflection sensitivity has been thoroughly discussed by many investigators. Cartwright (1) has given a treatment on the optimum design of both thermopiles and bolometers used with galvanometers when limited by Brownian movement near a critically damped galvanometer. In all of these discussions, the response has been assumed to be limited by the galvanometer period so that the response time of the detector was not important.

In 1947 Hornig and O'Keefe (4) published a summary of the theory of wire thermocouple design to secure, in addition to the highest sensitivity, the most rapid possible response. Rapid response was desired in order to make it possible to interrupt the radiation beam at a frequency high enough to allow of amplification and thereby eliminate the long period drift which has been mentioned as one of the major experimental difficulties.

If the blackened receiver changes its temperature by an amount θ due to absorbing radiation flux P (intensity $\times$ area) over a period of t, if the heat loss to the surroundings per sec. per degree of temperature change is L, and if the heat capacity of the system is C, then

$$C\frac{d\theta}{dt} + L\theta = P$$

$$C\frac{d\theta}{dt} = P - L\theta$$

$$\int_0^\theta \frac{d\theta}{P - L\theta} = \int_0^t \frac{dt}{C}$$

$$-\frac{1}{L}\ln(P - L\theta)/P = \frac{t}{C},$$

$$1 - L\theta/P = e^{-Lt/C}$$

$$\theta = P/L\ (1 - e^{-\lambda t})$$

Here $\lambda = L/C$ (1)

is the reciprocal of the time constant. As t approaches infinity, the equilibrium temperature increase is given by

$$\theta_\infty = P/L \qquad (2)$$

Therefore

$$\theta = \theta_\infty(1 - e^{-\lambda t}) \qquad (3)$$

Let Q be the thermoelectric power of the thermoelectric junction attached to the receiver. The relative voltage sensitivity, defined as e.m.f. generated per microwatt of radiation absorbed by the receiver after equilibrium, is given by

$$E = Q\,\theta_\infty/P = Q/L \tag{4}$$

The most important source of disturbances or noise in most cases is the Johnson noise resulting from the Brownian movement of electrons in the circuit resistance. This noise is quite accurately given by

$$\langle E_J^2\rangle_{AV.} = 4kTR\,\Delta\nu$$

where $\langle E_J^2\rangle_{AV.}$ is the mean square fluctuation e.m.f. in the frequency range $\Delta\nu$, k is Boltzmann's constant, T is the absolute temperature and R is the total circuit resistance. If R is given in ohms this becomes, at 300°K

$$E_J\,(\text{r.m.s.}) = 1.3 \times 10^{-4}\,R^{\frac{1}{2}}\,\Delta\nu^{\frac{1}{2}}\,\text{volt}$$

Then the minimum detectable power is given by

$$P_{min} = E_J/E = (4kTR)^{\frac{1}{2}}\,\Delta\nu^{\frac{1}{2}}/\,E$$

or

$$P_{min} = (4kT)^{\frac{1}{2}}\,\Delta\nu^{\frac{1}{2}}/S \tag{5}$$

where

$$S = E/R^{\frac{1}{2}} = Q/LR^{\frac{1}{2}}. \tag{6}$$

S is the only factor which depends on the design of the thermopile. According to Hornig and O'Keefe S is called the absolute sensitivity when the thermopile response time is short compared to the time in which changes in the intensity of the incident radiation may occur.

Let A = area of receivers,

κ = thermal conductivity of wire material,

ρ = resistivity of wire material,

a = cross-sectional area of wire,

l = length of individual wire,

σ = Stefan-Boltzmann constant,

L'= heat loss per sec per °C of heating other than by radiation or wire conduction,

and n = number of junctions.

If we denote the materials of the two wires by subscripts 1 and 2,

$$L = L' + 4\sigma AT^3 + n[\kappa_1(a_1/l_1) + \kappa_2(a_2/l_2)] \quad (7)$$

for both series and parallel thermopiles. For parallel thermopiles,

$$R = [\rho_1(l_1/a_1) + \rho_2(l_2/a_2)]/n \quad (8)$$

and for series thermopiles,

$$R = n[\rho_1(l_1/a_1) + \rho_2(l_2/a_2)] \quad (9)$$

To maximize S with respect to (a/l), let

$$\partial S/\partial(a_1/l_1) = 0, \quad \partial S/\partial(a_2/l_2) = 0 \quad (10)$$

Since, from Eq. (6),

$$dS = -(Q/2L^2R^{\frac{3}{2}})(LdR + 2RdL)$$

Equations (10) becomes

$$L\partial R/\partial(a_1/l_1) + 2R\partial L/\partial(a_1/l_1) = 0$$

$$L\partial R/\partial(a_2/l_2) + 2R\partial L/\partial(a_2/l_2) = 0$$

or, from Eq. (7), (8) and (9),

$$Ln\,\rho_1(l_1/a_1)^2 = 2Rn\,K_1$$

$$Ln\,\rho_2(l_2/a_2)^2 = 2Rn\,K_2$$

We obtain the optimum relation first found by Johansen:

$$(K_1/\rho_1)(a_1/l_1)^2 = (K_2/\rho_2)(a_2/l_2)^2 \qquad (11)$$

Under this condition, we have, for series thermopiles,

$$L = L' + 4\sigma AT^3 + n[K_1(a_1/l_1) + K_2(a_2/l_2)]$$

$$= L' + 4\sigma AT^3 + n\left[K_1\frac{a_1}{l_1} + K_2\frac{a_2}{l_2}\right] n\left(\rho_1\frac{l_1}{a_1} + \rho_2\frac{l_2}{a_2}\right)/R$$

$$= L' + 4\sigma AT^3 + \frac{n^2}{R}\left[K_1\rho_1 + K_2\rho_2 + K_1\rho_2\left(\frac{a_1 l_2}{a_2 l_1}\right) + K_2\rho_1\left(\frac{a_2 l_1}{a_1 l_2}\right)\right]$$

$$= L' + 4\sigma AT^3 + \frac{n^2}{R}\left[K_1\rho_1 + K_2\rho_2 + K_1\rho_2\left(\frac{\rho_1 K_2}{\rho_2 K_1}\right)^{\frac{1}{2}} + K_2\rho_1\left(\frac{\rho_2 K_1}{\rho_1 K_2}\right)^{\frac{1}{2}}\right]$$

$$L = L' + 4\sigma AT^3 + \frac{n^2}{R}\left[K_1\rho_1 + K_2\rho_2 + 2(K_1\rho_1 K_2\rho_2)^{\frac{1}{2}}\right]$$

$$L = L' + 4\sigma AT^3 + \frac{n^2}{R}\left[(K_1\rho_1)^{\frac{1}{2}} + (K_2\rho_2)^{\frac{1}{2}}\right]^2 \qquad (12)$$

or

$$S = nQ/\left\{L' + 4\sigma AT^3 + \frac{n^2}{R}\left[(K_1\rho_1)^{\frac{1}{2}} + (K_2\rho_2)^{\frac{1}{2}}\right]^2\right\}R \qquad (13)$$

Parallel thermopiles are equivalent to the case $n = 1$.

The optimum resistance, obtained by maximizing Eq. (13) with respect to R, is

$$R_{opt} = n^2\left[(K_1\rho_1)^{\frac{1}{2}} + (K_2\rho_2)^{\frac{1}{2}}\right]^2/(L' + 4\sigma AT^3). \qquad (14)$$

The maximum sensitivity is then

$$S = Q/2(L' + 4\sigma AT^3)^{\frac{1}{2}}\left[(K_1\rho_1)^{\frac{1}{2}} + (K_2\rho_2)^{\frac{1}{2}}\right]. \qquad (15)$$

This expression is independent of the number of junctions or whether they are arranged in series or in parallel. It is therefore the maximum possible absolute sensitivity. It should be noted that it is inversely proportional to the square root of the total receiver area. Hornig and O'Keefe suggest as a factor of merit for thermoelectric materials the quantity

$$M = Q/(K\rho)^{\frac{1}{2}}.$$

In comparing pairs of materials an exact factor of merit defined by

$$M' = (Q_1 - Q_2)/[(K_1\rho_1)^{\frac{1}{2}} + (K_2\rho_2)^{\frac{1}{2}}]$$

is used. A survey of the most favorable materials shows that semiconductor alloys have the best rating; however the properties of such materials might be hard to control because of extreme sensitivity to trace impurities.

In order to make fast response thermopiles, λ should be maximized without decreasing S. A straight forward way is to decrease the heat capacity, that is the dimension of all component parts, without decreasing S.

As a summary of the above discussion, it can be seen that a fast thermocouple for infrared spectroscopy should be designed as follows:

(i) Use the smallest possible receiver remembering that its length is limited by the width of the spectrum.

(ii) Use thermoelectric materials with highest factor of merit.

(iii) Use finest possible wires with length determined from Eq. (10) and (15).

(iv) Use one junction only as it should give results as good as any larger number of junctions.

CONSTRUCTION OF THERMOPILES

The Melloni thermopile, in use almost a century ago, consisted of blocks of bismuth and antimony, and in spite of its large heat capacity, rendered good service at that time. A thermopile having a faster action was made later by Rubens (10) in 1898 using fine wires of iron and constantan with hard solder junctions flattened for use as receivers. Lebedew (9) in 1902 observed that in an evacuated system the sensitivity of a thermoelement with a blackened receiver increased 7 times, while one with an unblackened receiver increased 25 times.

As previously mentioned, detailed descriptions of improved thermopile construction were published over the period from 1930 to 1934. Cartwright (1) described a thermocouple made of Hutchins alloys (Bi+Sb vs. Bi+Sn) (5) with the following characteristics: receiver area, 0.5 mm^2; resistance, 20 ohms; period, 1 sec.; sensitivity, better than 20μv/μwatt. The sensitivity is comparable with or better than that of most thermocouples made today.

As a result of these studies, the standard general type of thermocouple construction, as described in V. Z. Williams' paper (13), is as follows: The assembly consisted of 2 fine short wires (ca. 0.01-mm dia.) consisting of 97% Bi + 3% Sb and 95% Bi + 5% Sn (Hutchins alloys), respectively, which gives a thermoelectric coefficient of 120μv/^{o}C. These are spot welded at one end to form a junction and the other ends are soldered to heavy copper lead wires. The receiver, a piece of 0.1 to 1μ gold leaf blackened by painting with lampblack in lacquer or by low pressure evaporation, is cut to the size of the focused beam from the exit slit. This receiver is soldered to the junction by radiant heat, and two quartz fibers are added to support the receiver. An alternative procedure is to spot weld the receiver and wires and then lay the whole assembly on the quartz fibers before soldering to leads. Average characteristics of such thermocouples would be: receiver area, 6x0.4 mm; resistance, 10 ohms; period, 1 to 5 sec.; sensitivity 3 to 6μv/μwatt of incident radiation. Radiant power at the detector of a spectrometer for good resolution should be from 0.05 to 0.2μ watts.

Early work on fast, thin film (sputtered) thermocouples for a.c. use was carried out by Harris and his co-workers. These elements were not designed for spectrometer applications. Their resistances are as high as several thousand ohms. Roess and Dacus later reported evaporated thermocouples of Bi vs. Sb of the following characteristics: 20 to 50 ohms, a d.c. sensitivity of 6 to 7μv/10^{-4} watt per cm^2 and 50% response at 7 c.p.s.. Their sensitivity figure is difficult to compare with that of wire thermocouples because they are necessarily illuminating the entire thermocouple from hot to cold junctions in their test measurement while a wire thermocouple under similar test would see only the radiation intercepted by its receiver. An evaporated thermocouple of the type described can not have the d.c. sensitivity of a wire thermocouple because of its greater radiation loss from its larger area.

Hornig and O'Keefe (4) described some thermocouples built with 0.3 mm long leads of Hutchins alloys, with the characteristics: area, 0.5 mm^2; time constant, 0.036 sec.; d.c. sensitivity, 6.5 μv/μwatt; 88% response at 5 c.p.s.; minimum detectable signal at 5 c.p.s., 5×10^{-5} μwatts.

However, regardless of the discussions given above, as pointed out in Strong's "Procedures in Experimental Physics", the sensitivity of a thermopile depends on the skill exercised in its construction. Therefore, it is desirable to simplify the procedure so as to give a more dependable method.

In the first place, the thermoelectric materials in general are hard to solder and consistent results in soldering with radiant heat are even more difficult to attain. The present paper describes a method of making a single junction thermocouple by spot welding.

The housing of the thermocouple must provide a rigid support and hold a high vacuum. The latter condition indicates blown glass as probably most convenient. The design used is shown in Fig. 1.

The receivers are made of thin gold foil cut to size (about 0.5 by 7 mm) by a razor blade or scissors. Each is strengthened mechanically by folding: The receiver is placed between two sheets of thin bond paper. A straight edged piece of glass is placed on top with its edge accurately along the central line of the receiver. The plate is then pressed down, while the sheets of paper and the receiver are folded up and pressed against the straight edge with the flat tip of a minute spatula (see Fig. 2). A V-shaped receiver, with such a sharp crease is found to be stronger than one with a cylindrical curvature. A number of receivers are blackened simultaneously with bismuth black by evaporation in a vacuum (3).

Wires of Hutchins alloys are prepared by the Taylor process, melting the metals in an evacuated soft glass tube and drawing out both glass and metal to the desired diameter. The glass is removed with hydrofluoric acid and the thin metal wires carefully washed with water.

The circuit of the spot welder is shown in Fig. 6. The sliding contact on the 20K resistance serves to control the welding current. The secondary winding of the

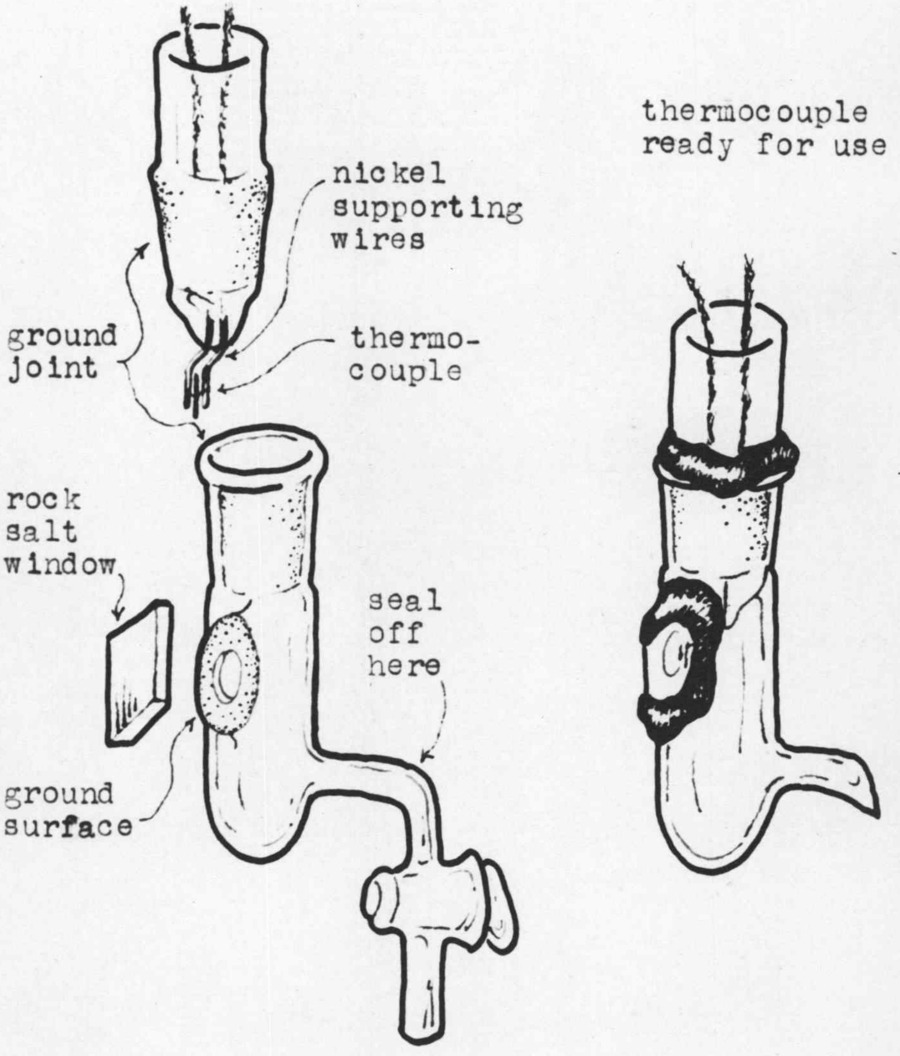

thermocouple
ready for use
nickel
supporting
wires
ground
joint
thermo-
couple
rock
salt
window
seal
off
here
ground
surface

Fig. 1.

transformer consists of a few turns of heavy copper wire terminating at two copper electrodes, which serve to apply the potential to the joint to be welded. The electrodes are brought in contact with the work, and a definite pressure, which can be adjusted by a counter weight on the upper electrode, is applied by means of a spring controlled by a foot pedal. The same foot pedal then also closes the discharging switch. The discharge of the condenser sends a current through the primary of the transformer for a small fraction of a second. The joule heat thus generated between the metal surfaces produces the weld.

The junction is constructed in the following way: A small wooden supporting table (a, Fig. 3) with a circular hole, large enough to admit the lower electrode of the spot welder, is set between the electrodes. The lower electrode underneath the table is raised until it is level with the table top. The thermoelectric wires are laid on the table as shown in a and b Fig. 3. The pressure between the electrodes is adjusted so that they hold the wires lightly without breaking them. On closing the switch, a very small current is used to start with, and gradually increased until a very good junction is established. No flux is used.

A blackened receiver is laid across the junction as shown in c Fig. 3. The current is again reduced to a

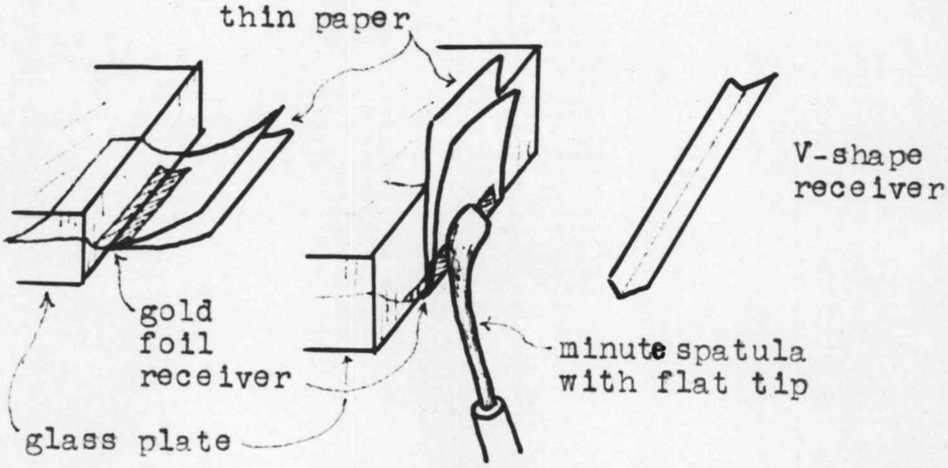
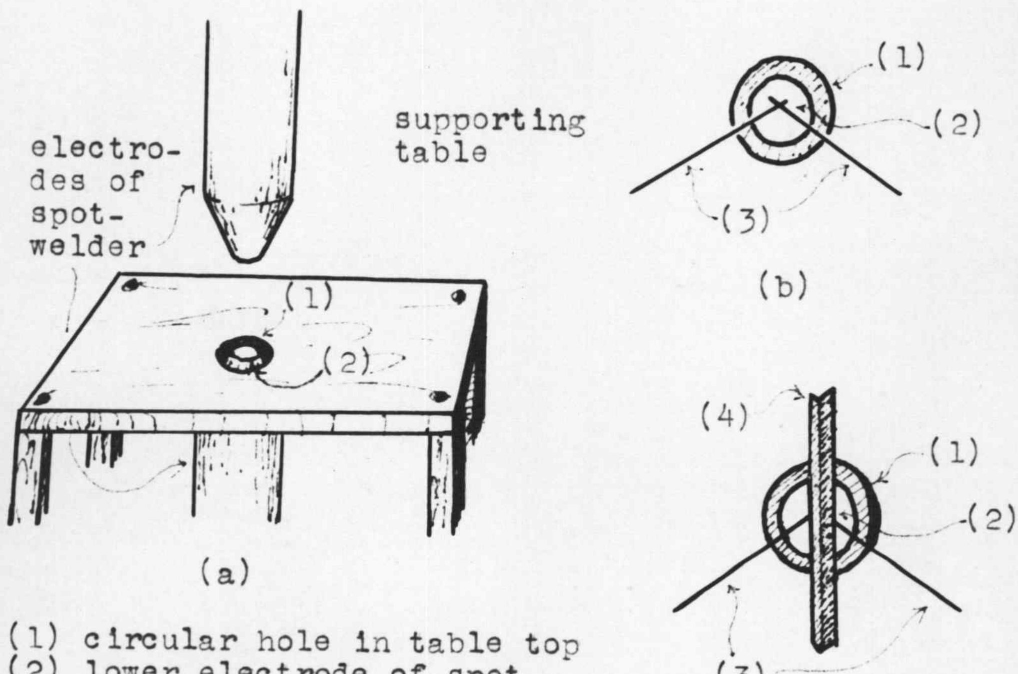


Fig. 2.



(1) circular hole in table top
(2) lower electrode of spot-welder
(3) thermoelectric wires
(4) blackened receiver

Fig. 3.

small value and the weld made in the same manner as before. The two nickel leads on the housing, (Fig. 1) are bent so that the distance between them is equal to the desired length of the thermocouple. The housing is placed so that one of the nickel leads lies on the thermocouple on the lower electrode of the spot welder (Fig. 4). The glass stem is held very steadily against the supporting table and the weld is made with a current about 8/5 of the value formerly used. The supporting table is removed and the stem turned so that the thermocouple faces upward. The same lead is welded at one or two additional points, using a little more current; see B and C, Fig. 5. The loose end of the lead is broken off at C by bending it down further around the supporting wire. The other lead is then welded to its supporting wire in a similar manner.

The thermocouple is placed inside the housing and the ground joint carefully sealed. The tube is then evacuated to as high a vacuum as possible. For maintaining a high vacuum, activated charcoal or fresh calcium filings may be placed in a side tube and baked while the tube is being evacuated.

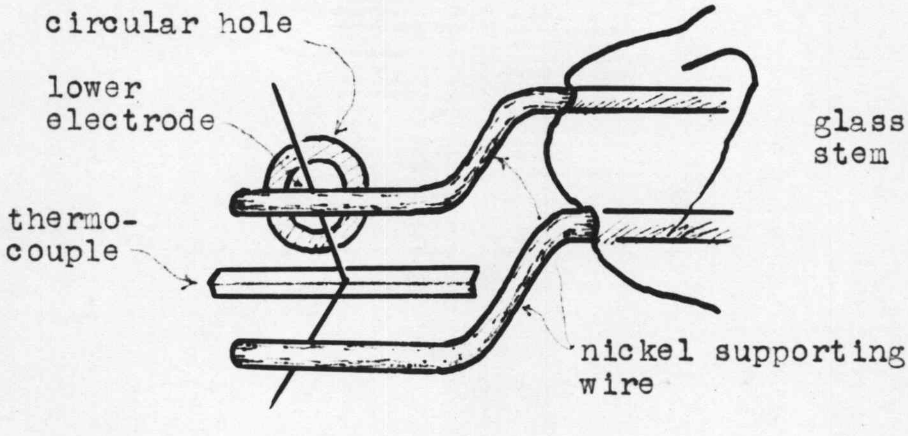


Fig. 4.

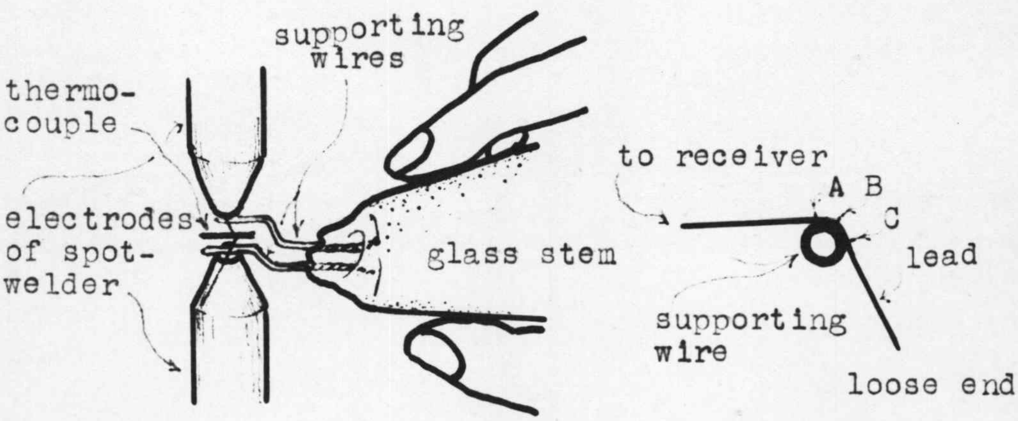


Fig. 5.

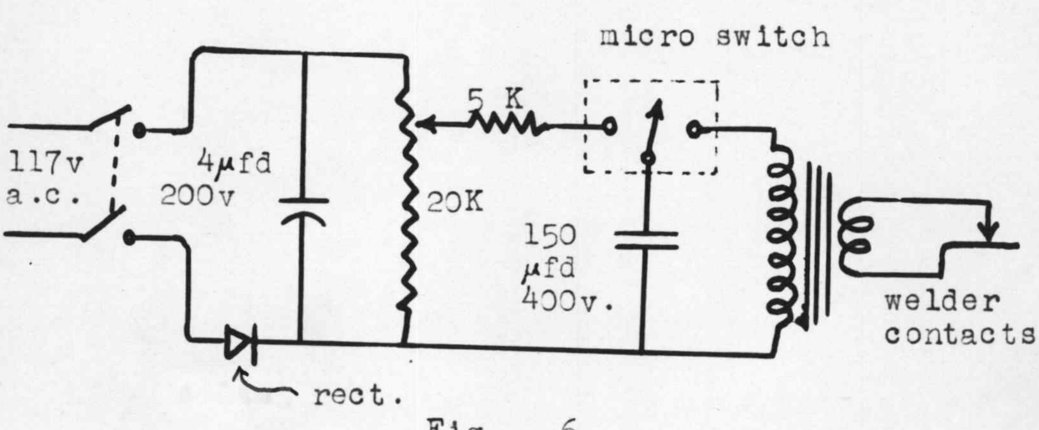


Fig. 6.

SUMMARY

The thermocouple built has the following characteristics:

Dimensions of receiver: 7 mm × 0.5 mm.

Properties of leads:

Alloy	Diameter (mm)	Length (mm)	Conductivity $\left(\frac{watt}{cm\,^{\circ}C}\right)$	Thermoelectric power $\left(\frac{\mu volts}{^{\circ}C}\right)$
95% Bi, 5% Sn	0.035	2.7	0.045	-75
97% Bi, 3% Sb	0.085	2.0	0.07	+30

Theoretical equilibrium voltage sensitivity, assuming the heat lost by other means than radiation and conduction equal to zero,

$$E = Q/L = Q/\{4\sigma A T^3 + [K_1(a_1/l_1) + K_2(a_2/l_2)]\}$$
$$= 2.4\ \mu\text{volts}/\mu\text{watt}.$$

Allowing 10% loss by reflection from the rock salt window in front of the thermocouple, the expected voltage sensitivity will be 2.2 μvolts/μ watt. Experimentally using a 40 watt incandescent lamp 119cm from the thermocouple and assuming that the receiver absorbs all the energy incident upon it, the galvanometer deflection for the best thermocouple was 51.7 mm at a scale distance of 1 meter. This gives the relative voltage sensitivity, E, as 1.9 μ volts/μ watt. This value is approximately 86% of the theoretical value and indicates excellent performance. The method of making radiation thermocouple by welding is reproducible after some skill has been developed.

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