# NOISE, TEMPERATURE COEFFICIENT, AND LONG TIME STABILITY OF ELECTRODES FOR TELLURIC OBSERVATIONS*

G. PETIAU and A. DUPIS**

### ABSTRACT

PETIAU G. and DUPIS A. 1980, Noise, Temperature Coefficient, and Long Time Stability of Electrodes for Telluric Observations, Geophysical Prospecting 28, 792–804.

Numerous electrodes, already used in geophysics or just perfected by us, have been compared by measuring the three main characteristics which interest the user: noise spectrum, temperature coefficient and polarization with its stability versus time.

Among the most used unpolarizable electrodes, silver–silver chloride (Ag–AgCl) are the best ones. But a systematic research of all different possible metal-salt couples, have led us to use lead–lead chloride (Pb–PbCl$_2$) for the following reasons: noise as low as the one of Ag–AgCl at 1 Hz and even lower for the low frequencies (0.4 $\mu$V at 1 Hz and 1.2 $\mu$V at 0.01 Hz for peak to peak value and $\Delta F = F$), temperature coefficient about ten times weaker ($-40\ \mu$V/°C instead of $-450\ \mu$V/°C) and also better long time stability of the polarization (1 mV/month instead of 2 at 10 mV/month).

We have been using these electrodes since 1977 as "tube" electrodes which are very easy to use. They allow us to record correctly the fast variations thanks to their low noise, the very slow variations, their low temperature coefficient and their stability, and this with telluric lines only about 100 m long.

## 1. MEASUREMENT OF ELECTRODE NOISE

### 1.1 Definition and expression of the noise

The purpose of an electrode is to give the potential of the medium where it has been placed; thus it must transmit the potential of an ionic conductor, here the soil, to an electronic conductor, the metallic wire of the line. This contact between electrolytes and metal creates additional potentials. If these are kept constant they do not disturb the measurement of the variations of

---

potential *differences* between the two electrodes of a telluric line. If they are not stable, their differential variations can be confused with the signal, and this constitutes the "noise" that we have measured on different types of electrodes.

Generally, noise is expressed as a noise density in $\sqrt{\text{Hz}}$. Though we can compare the noise of two devices at a given frequency, this is not immediately possible at different frequencies, because a fixed band width $\Delta F$ does not have the same physical significance at different frequencies. It is much more logical to use a constant relative band width $\Delta F/F$. If one chooses $\Delta F = F$ and requires $F_1 : F = F : F_2$ and $F_2 - F_1 = F$, we have $F_1 = 0.62\ F$ $F_2 = 1.62\ F$.

For all our measurements we have expressed the noise as peak-to-peak value for a band width $\Delta F = F$.

A very interesting practical advantage is that the noise expressed in that way gives directly the inaccuracy of the signal peak-to-peak measurement at the given frequency.

Let us note that the noise expressed as peak-to-peak value for $\Delta F = F$ and the customary noise density are connected by

$$\text{Noise}(V_{pp}, \Delta F = F) = \text{Noise}(V_{\text{rms}}\ \Delta F = 1\ \text{Hz})2\sqrt{2}\sqrt{F}.$$

## 1.2 Noise of a Telluric recording device

To measure in use the noise of a telluric recording device including electrodes, lines, and amplifier, we must eliminate the natural variations of the telluric field. For this, we use two parallel lines of the same length and we find the difference of the two signals after amplification. If the two amplifiers have exactly the same amplification coefficient and dephasing, there only remains the noise of the two devices, and we obtain the noise of a device by dividing by $\sqrt{2}$ (because the noises are aleatory and independent, they are added quadratically).

We have shown elsewhere (Petiau 1976) that when we diminish as far as possible every noise source of the recording device, it is the noise of the electrodes which remains the most important. To obtain this, the following care must be taken:

*Noise of the amplifier.* As the noise of good electrodes is low, about a few $\mu$V, we must use a very good amplifier. This must have a differential input with high impedance, therefore we use at the first stage very low noise operational amplifiers (OP05 or AD510).

*Removal of high frequencies.* It is necessary to eliminate frequencies above the frequency band used before the signal enters the amplifier. These frequencies always exist on a telluric line (HF, atmospherics) and can create by non-

linearity and intermodulation low frequency disturbances that are stronger than the noise of the electrodes.

*Disturbance of the lines.* If the telluric lines are placed loosely on the ground, the wind can make them oscillate. So some e.m.f. of about ten $\mu V$ appear mainly by induction in the earth's magnetic field. It is necessary to bury the wire, or make the measurement when there is no wind.

## 1.3 A method of measurement of the electrodes noise

To measure only the noise of the electrodes, it is not necessary to use the above method which requires two channels identical within about 1% and four electrodes of the same type. We have found a simpler method that gives the same results. The measurement is made in a laboratory with only two electrodes at a distance of 10–20 cm in a box full of earth, or salted clay to reduce the contact resistances. In this arrangement only the amplifier noise is added, and its spectrum can be eliminated by comparing all measurements of noise.

To avoid an abnormal scattering, the measurement must be done at specified times after placing the electrodes. In fact, the noise decreases with time and the stabilization is different depending on the type of electrodes.

## 1.4 Noise and time stability of various electrodes

Numerous types of electrodes are used in geophysics, for our measurements, we have chosen some electrodes which can be divided into three groups: (a) metallic electrodes (brass and steel stakes), (b) graphite electrodes and (c) unpolarizable electrodes (copper, cadmium, silver, mercury, and lead).

Figs 1 and 2 show the noise of electrodes $\frac{1}{2}$ to 1 h after placement and 24 h after placement, respectively, to indicate the stabilization. For all electrodes, the noise decreases with the frequency, and for frequncies higher than 10 Hz, the amplifier noise becomes more important than that of the electrodes.

*Brass and steel electrodes.* These electrodes are simple and strong, but their noise is significant, e.g. at 0.01 Hz, about 10 $\mu V$ after $\frac{1}{2}$ to 1 h and 4 $\mu V$ after 24 h. These electrodes take a long time to become stable. Wetting with water or with a copper sulphate solution diminishes the contact resistance with the soil considerably but increases the noise, and we must wait 24 h to obtain the minimal noise. But for frequencies above 10 Hz, amplifier noise is predominant and since the noise of these electrodes is not much different from the other electrodes, they should be employed for their operational simplicity.
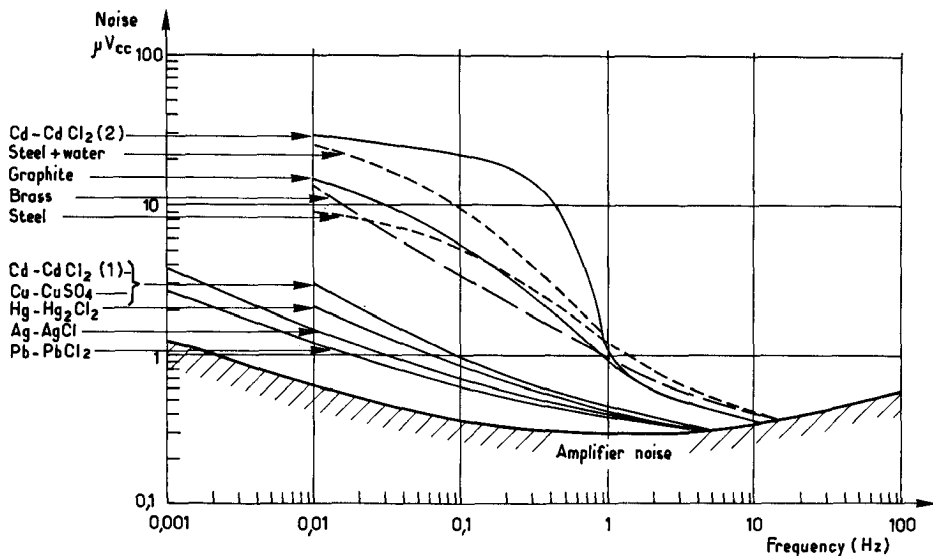
Fig. 1. Noise of different electrodes $\frac{1}{2}$–1 h after setting up.

*Graphite electrodes*. This type of electrode has been used for telluric measurements in the sea. Graphite, is a non-metallic electronic conductor, is not of interest for noise reduction studies. The noise remains very high (13 $\mu$V at 0.01 Hz) even after 24 h of stabilization.

*Copper–Copper sulphate electrodes* $(Cu–CuSO_4)$. These are the first unpolarizable electrodes used in geophysics. The solution is contained in a porous vessel to ensure the contact with the soil. Our measurements have been made with electrodes where the solution was fixed in an agar-agar gel or in a clay paste in a small insulated container open on one side. The noise is smaller (3 $\mu$V at 0.01 Hz) and the time of stabilization after placement to obtain minimal noise is about 1 h.

*Cadmium–Cadmium chloride electrodes* $(Cd–CdCl_2)$. In a model currently used in geophysics, the cadmium stick and the saturated solution (chloride or sulphate) are contained in a small vase with a bottom made of porous porcelain to ensure the contact with the soil. The noise is also small (the curve "cadmium 1" of fig. 1 is identical to that for $Cu–CuSO_4$). But in some cases we have observed an abnormal behaviour (curve "cadmium 2" of fig. 1). We can see in the recordings some quick variations of 20–40 $\mu$V, sometimes even more, which seem to be connected to the liquid electrolyte. The reasons could be the release of small air bubbles from the metallic electrode, the presence of a triple contact electrolyte-air-metal when the vase is not completely full, or sudden variations of flow in the porous porcelain (which modify the electrofiltration potential). Meunier (1962) notes identical effects with copper–
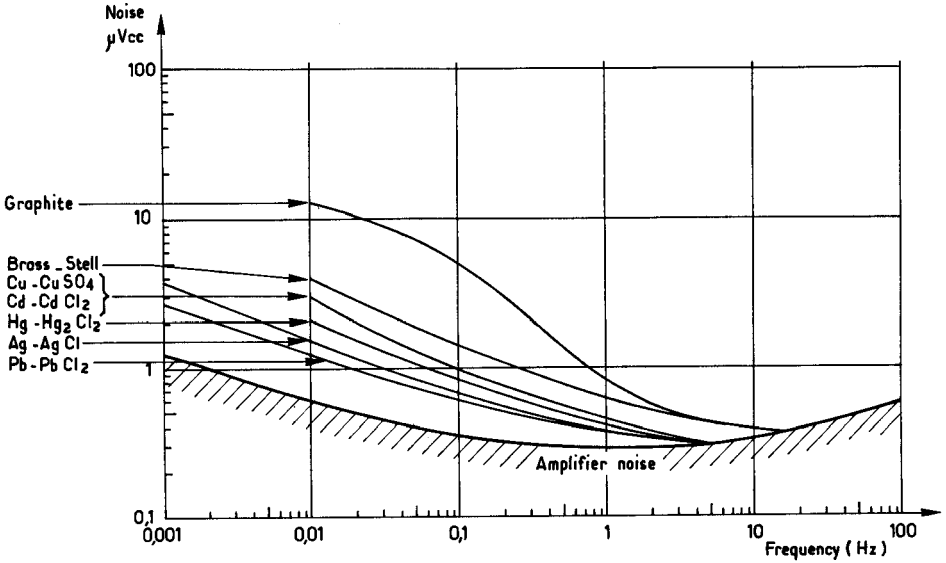
Fig. 2. Noise of the electrodes 24 h after setting up.

copper sulphate electrodes with liquid electrolyte. These disturbances were eliminated by fixing the electrolyte in an agar-agar gel or in clay, yielding again the curve "cadmium 1"; in this case, the stabilization is much quicker: about 1 h instead of 24 h.

*Silver–Silver chloride electrodes* (*Ag–AgCl*). These are used as reference electrodes (Ives and Janz 1961) and have been adapted to geophysical measurements by Meunier (1965) and Filloux (1967, 1973). A silver wire is covered with silver chloride by electrolysis, then it is set in an agar-agar gel (or in clay) saturated with sodium chloride, mainly to ensure the conduction because the silver chloride is a barely soluble salt. The whole is placed in a cloth bag or in an insulated maintenance box opened on one side to ensure solidity without preventing the contact with the soil. Munaut (1973) and Hempfling (1977) have described such electrodes in which the salt concentration decreases from the center to the outside of the electrode. Potassium chloride is used in place of sodium chloride to reduce the diffusion potential. This potential is due to the difference between the velocities of cations and anions at the separation of the two media when the concentrations are different. $K^+$ and $Cl^-$ ions have very similar velocities than $Na^+$ and $Cl^-$ ions. However, we have not found any significant experimental difference for the time of stabilization between the two salts.

Figs 1 and 2 show that the electrodes Ag–AgCl have very low noise (1.5 $\mu$V at 0.01 Hz) and that they stabilize very quickly ($\frac{1}{2}$–1 h).

*Calomel electrodes* $(Hg–Hg_2Cl_2)$. These are also used as reference electrodes in laboratories. A platinum wire is in contact with a drop of mercury covered with mercurous chloride. We have modified them by placing the mercury and the mercury chloride into a tube filled with an agar-agar gel saturated with potassium chloride. The minimal noise is low (2 $\mu$V at 0.01 Hz), but we have also observed some higher values, perhaps due to instabilities at the contact between the liquid mercury and the mercurous chloride.

*Lead–Lead chloride electrodes* $(Pb–PbCl_2)$. Lead plates have been used for a long time as electrodes. We have developed unpolarizable electrodes using $Pb–PbCl_2$ which have very interesting qualities. They are made of a lead wire placed in a container filled with plaster prepared with water saturated with $PbCl_2$ (15 g/1) and NaCl (360 g/1). At low frequencies, the noise (1.2 $\mu$V at 0.01 Hz) is as low or even lower than that of Ag–AgCl electrodes. They also stabilize very fast: $\frac{1}{2}$–1 h.

### 1.5 Conclusion for the noise and the stabilization

For the noise below 10 Hz and for the stabilization time, this comparison shows a clear superiority of the unpolarizable electrodes with the electrolyte fixed in an absorbing material. In fact, with such electrodes the contact between the soil and the metal is done in two well separated steps: The first metal-electrolyte contact which produces generally significant potentials (about 0.1–1 V) is well stabilized because the concentrations are fixed and protected in the center of the electrode. The second contact, between the electrolytes of the soil (with variable nature and concentration) and those of the electrode, is not critical because the potentials are much lower, around a few mV for the diffusion with which one is mainly concerned here.

Among the metal-salt combinations we point out Ag–AgCl and $Pb–PbCl_2$, which are particularly interesting. However, we have measured strong noise for lead–lead nitrate and antimony–antimony trichloride couples (5–15 $\mu$V at 0.01 Hz). and even stronger noise with tin–tin chloride (100–200 $\mu$V at 0.01 Hz).

## 2. TEMPERATURE COEFFICIENT OF THE ELECTRODES

### 2.1 Theoretical study of the temperature coefficient

The potential of an electrode made of a metal placed into a solution of one of its salts, is given by Nernst's formula:

$$E = E_0 + \frac{RT}{n\text{F}} \ln \{M^{+n}\} \tag{1}$$

$E_0$–standard potential (at 25°C for $\{M^{+n}\} = 1$) given by chemical tables

R–constant of the perfect gas
T–absolute temperature
F–Faraday constant
$n$–metal valency

$$\left.\begin{array}{l} \\ \\ \\ \end{array}\right\} \quad \frac{RT}{F} = 0.0257.$$

$\{M^{+n}\}$ Metal ion activity, which we replace in the following for reasons of simplicity by the concentration.

The potential of this electrode cancels itself for a certain value of ion concentration in the solution, we call this the equilibrium concentration $\{M^{+n}\}_{eq}$:

$$E = 0 = E_0 + \frac{RT}{nF} \ln \{M^{+n}\}_{eq}$$

from which

$$E_0 = -\frac{RT}{nF} \ln \{M^{+n}\}_{eq}. \tag{2}$$

The potential of the electrode thus becomes:

$$E = \frac{RT}{nF} \ln \frac{\{M^{+n}\}}{\{M^{+n}\}_{eq}} \tag{3}$$

where the equilibrium concentration deduced from (2) is:

$$\{M^{+n}\}_{eq} = e^{-nFE_0/RT}. \tag{4}$$

To obtain the temperature coefficient, one has to derive (3) with respect to $T$; $\{M^{+n}\}$ and $\{M^{+n}\}_{eq}$ are also functions of temperature, and we obtain:

$$\frac{dE}{dT} = \frac{E}{T} + \frac{RT}{nF} \left[ \frac{\{M^{+n}\}'}{\{M^{+n}\}} - \frac{\{M^{+n}\}'_{eq}}{\{M^{+n}\}_{eq}} \right] \tag{5}$$

where

$$\{M^{+n}\}' = \frac{d}{dT} \{M^{+n}\}.$$

If the electrode is of the second kind, that is to say if the salt $(MX_n)$ is a sparingly soluble salt, the concentration of the ions $M^{+n}$ is defined by the relation $\{M^{+n}\} = K_s/\{X^-\}^n$ where $K_s$ is the constant of solubility and $\{X^-\}$ is the total concentration of $X^-$ ions in the solution coming from the salt of the metal or from other salts having this common ion; the temperature

coefficient becomes:

$$\frac{dE}{dT} = \frac{E}{T} + \frac{RT}{nF}\left[\frac{K'_s}{K_s} - \frac{n\{X^-\}'}{\{X^-\}} - \frac{\{M^{+n}\}'_{eq}}{\{M^{+n}\}_{eq}}\right]. \tag{5bis}$$

The terms with $K'_s$ and $\{X^-\}'$ or $\{M^{+n}\}'$ are due to the variations of the solubility of the salts (if the solutions are saturated) and also due to the variations of the activity. The term containing $\{M^{+n}\}'_{eq}$ is important and is determined by the nature of the metal. The term $E/T$ is important because it may be varied by adjusting the concentration of the ions of the metal. In this way the temperature coefficient can be made to become zero around the average temperature of the electrodes.

## 2.2 Comparison of the temperature coefficients of various metal–salt couples

Obviously, the suitable metals are those whose salts allow to get concentrations close enough to their equilibrium concentration. In the scale of the standard oxydo-reduction potentials, the latter considerations lead us to retain the metals set between silver (with sparingly soluble salts) and cadmium (with very soluble salts). Table 1 sums up our measurements of the temperature coefficients at 25°C; note that silicium and germanium, which we have not been able to test, could also be interesting because of their good situation in the standard potential scale.

The electrodes are defined by the metal, the salt of the metal, eventually a complementary salt which modifies the concentration of the ions of the metal or which ensures conduction, and the material fixing the electrolytes.

We have measured the temperature coefficient of some electrodes with different concentration of the ion of the metal, to determine approximately

Table 1. *Temperature coefficient of the electrodes.*

| Electrode | | Equilibrium-concentration mol/1 | Metal concentration mol/1 | Temperature coef. at 25°C $\mu V/°C$ |
|---|---|---|---|---|
| Ag–AgCl | NaCl sat. clay | $3.1 \cdot 10^{-14}$ | $2.8 \cdot 10^{-11}$ | $-410$ |
| Hg–Hg$_2$Cl$_2$ | KCl sat. | $2.1 \cdot 10^{-27}$ | $8.8 \cdot 10^{-20}$ | $-660$ |
| Cu–CuSO$_4$ | clay | $2.2 \cdot 10^{-12}$ | $1.4$ | $-360$ |
| Sb–SbCl$_3$ | clay | $4.4 \cdot 10^{-8}$ | $43.8$ | $-320$ |
| Pb–PbCl$_2$ | NaCl sat. plaster | $1.8 \cdot 10^4$ | $1.55 \cdot 10^{-6}$ | $-40$ |
| Pb–Pb(C$_2$H$_3$O$_2$)$_2$ | Agar-agar | $1.8 \cdot 10^4$ | $1.88$ | $+100$ |
| Sn–SnCl$_2$ | clay | $3.9 \cdot 10^4$ | $\simeq 14$ | $\simeq +200$ |
| Cd–CdCl$_2$ | clay | $3.9 \cdot 10^{13}$ | $7.33$ | $+460$ |

the concentration which would give a zero coefficient; we have obtained:

Ag–AgCl      Conc. $Ag^+$ $8 \cdot 10^{-10}$      Conc. NaCl 0.227
Hg–$Hg_2Cl_2$      Conc. $Hg_2^{++}$ $4.2 \cdot 10^{-23}$      Conc. KCl $2 \cdot 10^{-3}$
Pb–$PbCl_2$      Conc. $Pb^{++}$ $1.4 \cdot 10^{-4}$      Conc. NaCl 0.423

For copper, a $Cu^{++}$ concentration much higher than possible would be necessary.

Antimony and tin electrodes are not interesting because their noise is too high. Cadmium, which has a strong positive temperature coefficient, would require a very low concentration of $Cd^{++}$ ions.

Nevertheless, one should check that the use of non-saturated solution to cancel the temperature coefficient does not involve drift by loss of stability of the electrodes. In fact, oversaturated solutions (with salt in excess) allow the concentrations to be kept constant even under difficult conditions as are frequently encountered in geophysics. For this reason we will use the Pb–$PbCl_2$ electrodes saturated with NaCl (or KCl) which have a tempera-ture coefficient ten times lower than that of the Ag–AgCl electrodes currently used. We have not found any difference in the temperature coefficient (or the noise) when using ordinary lead instead of very pure lead.

### 3. POTENTIAL DIFFERENCE OF POLARIZATION OF THE ELECTRODES

#### 3.1 Potential difference of polarization of various electrodes

The potential difference between electrodes is the continuous or very slowly variable voltage which appears between two electrodes of the same type placed (as for the measurement of the noise) at a short distance of one another in a suitable substratum (tank containing damp earth or salted clay). For two identical electrodes, the polarization should therefore be null.

With metallic and graphite electrodes, the polarization is variable enough: about 10–25 mV; on the other hand, for unpolarizable electrodes (copper, cadmium, silver, mercury and lead) the values are only of a tenth of a mV to a few mV.

#### 3.2 The potential difference of polarization as a function of time

We have observed the variations of polarization of 20 Ag–AgCl electrodes during two years and of 50 Pb–$PbCl_2$ electrodes during a year and a half (fig. 3). In each case one electrode was used as reference. Some of the elec-
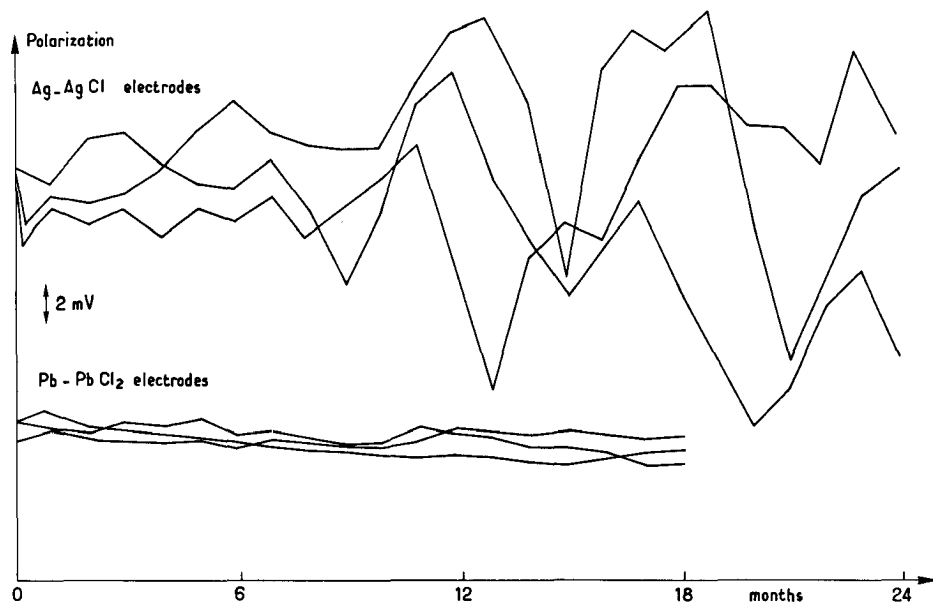
Fig. 3. Variation of the potential difference of polarization of a few Ag–AgCl and Pb–PbCl₂ electrodes (in each case, one electrode is used as reference).

trodes in each set have abnormal polarizations. For the others, after a few days of stabilization following their fabrication, the potential difference of polarization of the Ag–AgCl electrodes varies at about 2 mV per month. After approximately 9 months they became more unstable with variations of 10 mV per month or more; it is possible that the silver chloride layer becomes spoiled with time. Let us note however, that the noise has not appreciably changed. For Pb–PbCl₂ electrodes the stability is very good, about 1 mV per month. No change was observed after one and one half years of control.
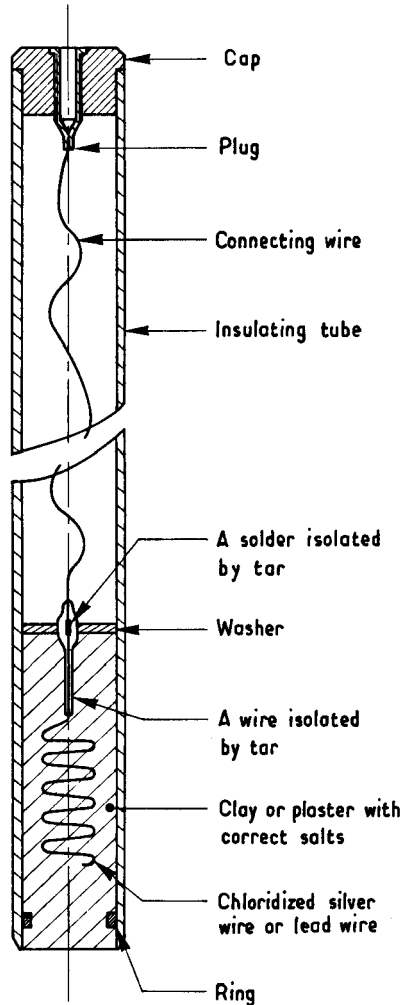
## 4. TUBE ELECTRODES

In this Section we describe a special mechanical realization of unpolarizable electrodes, independent of the chosen metal-salt couple.

### 4.1 Researched qualities and realization

To be used in the best conditions, the electrodes must have some other qualities which we are going to try to realize here: (a) convenient placement and recovery, (b) good mechanical resistance to all manipulations, (c) good

electrical contact with the soil ensured at the lower part of the electrode only, and (d) minimal disturbance of the soil by placing the electrode.

This has led us to use a plastic tube (PVC diameter 21–25 mm) which serves as a support and protects the electrode itself (fig. 4). Two lengths have been used: 40 cm to record periods less than a few minutes, and 60 cm to record long periods. At the lower part of the tube, we placed the metal covered with clay or plaster saturated with suitable salts. The solder is care-



Cap

Plug

Connecting wire

Insulating tube

A solder isolated by tar

Washer

A wire isolated by tar

Clay or plaster with correct salts

Chloridized silver wire or lead wire

Ring

20mm    Length 400 mm or 600 mm

Fig. 4. Design of the "tube" electrodes.

fully covered with tar (hot-laid) so that only the metal of the electrode is in contact with the electrolyte. A plug allows the connection at the upper part of the tube.

When they are not used, these electrodes must be kept in a plastic container, the active extremity lying on a synthetic sponge impregnated with salted water to avoid dehydratation.

## 4.2 Placement

A cylindrical hole 25 or 50 cm deep (depending on the electrode) is dug, with a jumper bar having the diameter of the electrode. This has the advantage of not disturbing the soil too much, and of compacting the soil on the sides of the hole, 5–10 cm³ of salted clay is then poured into the hole, half saturated with NaCl, forming a base into which the electrode is set by hand. The mud ensures a good contact; and a transition of concentration between the electrode and the soil.

The internal resistance of one electrode is 30 Ω and the total resistance between two placed electrodes changes from a few hundred to a few thousand Ω depending on the soil.

## 4.3 Results

With the "tube" electrodes we have found noise similar to that of the "bag" or "box" electrodes described above. However, in addition to their convenience in use, the stabilization time to obtain minimal noise is very low, less than a quarter of an hour, because of the reduced disturbance of the soil during placement.

## 5. CONCLUSION

We repeat in this study some results of measurements comparing, in a precise way, the main characteristics of different electrodes (already used or new) to measure the earth's electrical field.

For frequencies higher than 10 Hz, the amplifier noise is at present predominant. The problem is not one of the electrodes, and if one is only interested in these frequencies, simple metallic stakes will be easiest to use. For frequencies less than 10 Hz and down to periods of a few minutes, Ag–AgCl and Pb–PbCl$_2$ electrodes are more suitable because of their low noise. Finally, for periods of 5–10 min and up to daily or pseudo-continuous variations, Pb–PbCl$_2$ electrodes should be chosen because of their very low temperature coefficient and their long time stability.

We use $Pb$–$PbCl_2$ electrodes for magnetotelluric measurements in the field in the whole range going from the diurnal variation to 100 Hz. With these electrodes (and with the right precautions to eliminate the other disturbances noted in 1.2) 100 m long telluric lines are long enough to record the natural signals with a signal-to-noise ratio (for a mean activity) of about 10 at 1 Hz and 30–40 at 0.01 Hz. Still using the same length of line, the diurnal telluric variation is about 200 $\mu$V (2 mV/km). The differential variations of temperature of two electrodes set 50 cm deep are about 0.1–0.2°C (for a daily $\Delta T$ of 15°C at the surface) and involve therefore a thermal drift of 5–10 $\mu$V, that is 20–40 times smaller than the signal.

## REFERENCES

FILLOUX J.H. 1967, Oceanic electric currents, geomagnetic variation and the deep electrical conductivity structure of the ocean-continent transition of the central California. Ph.D Theses, Univ. of Calif. San Diego.

FILLOUX J.H. 1973, Techniques and instrumentation for study of natural electromagnetic induction at the sea. Physics of the Earth and Planetary Interiors 7, 323–338.

HEMPFLING R. 1977, Beobachtung und Auswertung tagesperiodischer. Variationen des erdelektrischen Feldes in der Umgebung von Göttingen. Dissertation Univ. Göttingen.

IVES D.J.G. and JANZ, G.J., 1961, Reference electrodes, New York, Academic Press.

MEUNIER J. 1962, Contribution à l'étude expérimentale des problèmes d'enregistrement électro-telluriques et à l'amélioration des techniques de prospection. Thèse 3ème cycle. Faculté des Sciences Paris. Laboratoire Géophysique Appliquée.

MEUNIER J. 1965, Enregistrement tellurique en mer. Bulletin de l'Institut Océanographique. Monaco 65, 1339–1965.

MUNAUT M. 1973, Etude d'un nouveau type d'électrode impolarisable. Diplôme d'ingénieur géophysicien. I.P.G. Strasbourg.

PETIAU G. 1976, Etude spèctrale du bruit et de diverses causes de perturbation affectant l'enregistrement du champ électrique tellurique dé 0.01 Hz–CRG/MTT Garchy–Nièvre.