An electrode technique for measurement of chloride concentration in microsamples

Robert K. Popp[1], John D. Frantz

Geophysical Laboratory
Carnegie Institution of Washington
Washington, D. C. 20008

and Gerald L. Vogel

American Dental Health Association
Health Foundation Research Unit
National Bureau of Standards
Washington, D. C. 20234

Abstract

A simple device is described for adapting a chloride solid-state electrode for microliter volumes. The device, which consists of a nylon cylinder in which 4 holes are drilled, is waxed onto the surface of an inverted chloride electrode. Samples of 1–5 μl are deposited in the holes of the adapter and a KNO_3–agar filled glass capillary is used to make contact between the samples and a reference electrode.

Introduction

Experimental studies using the Ag–AgCl buffer as a monitor for either hydrogen fugacity (Chou, 1978) or for HCl^0 concentration (Frantz and Popp, 1979) require accurate and precise measurement of chloride ion concentrations in microvolume samples (1–10 μl). The Buchler chloridometer has proven adequate for samples in which the concentration of Cl^- is greater than 0.01 mole/liter. This report describes a new technique for measurement of Cl^- in microsamples in the concentration range 0.01 to approximately 0.0001 mole/liter chloride.

Experimental procedure

Vogel and Brown (1979) have recently described the adaptation of a commercial solid-state electrode for measurement of fluoride concentration in microvolume samples of 1 to 5 μl. The method described here employs a double-junction reference electrode modification of that technique for measuring chloride concentration. A commercial chloride electrode (Orion Model 94-17) is modified for small volumes by clamping the electrode in an inverted position and

applying a thin coat of red dental wax to its sensing element. A 12.5mm-diameter by 5mm-thick nylon disc, through which four 2mm holes have been drilled, is then affixed to the electrode by gently heating it on a low-temperature hot plate and pressing it onto the wax-covered surface of the electrode. Wax in the holes of the adapter is then removed with a small piece of cotton wrapped around a toothpick and soaked in chloroform. The holes of the adapter serve as sample compartments with a wax seal between samples (Fig. 1).

A miniature reference electrode for use with the modified chloride electrode is constructed as follows: a heavy-walled Pyrex tube (8 mm O.D. by 1.3 mm I.D.) is pulled to an inner diameter of 0.10 to 0.15 mm. A section of this tube is then pulled again to an I.D. of 0.03 to 0.01 mm and cut to form a tapered end (Fig. 1). This microcapillary is then connected to a tapered glass tube attached to the bottom of a two-neck distillation flask. The flask, tube, and tip assembly are filled with a warm 1.0 mole/liter KNO_3 solution containing ~0.2 wt% agar (Fig. 1). The exact agar concentration to be used is determined by the dimensions of the capillary tip. A solution containing too little agar will leak through the capillary tip, whereas one containing too much agar will pull away

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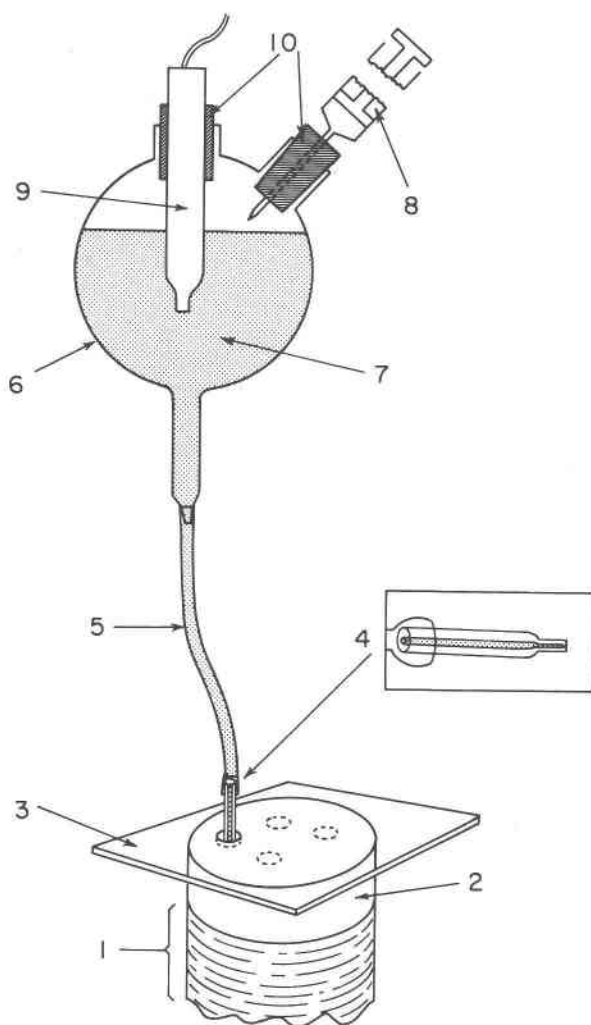[1] Present address: Department of Geology, Texas A & M University, College Station, Texas 77843.

Fig. 1. Configuration of chloride electrode: (1) solid state chloride electrode; (2) nylon adapter; (3) plastic microscope cover slide; (4) microcapillary tip; (5) plastic tubing; (6) 2-neck distillation flask with tapered glass tube attached; (7) 1.0 mole/liter KNO_3 solution with 0.2 wt% agar; (8) syringe; (9) calomel reference electrode; (10) rubber stoppers.

from the end of the tip and break electrical contact. Electrical contact may be restored by pressurizing the solution *via* a syringe inserted through a rubber stopper in one neck of the flask. A calomel reference electrode is inserted into the solution by means of a rubber stopper in the second neck of the flask. Finally, both the reference and chloride electrodes are connected to a pH meter or electrometer.

Samples are introduced into the holes in the adapter with an Eppindorf-type micro-pipetter with disposable plastic tips. The presence of air bubbles at the base of a hole will interfere with the electrical

contact, and thus care is required in the pipetting. After loading the adapter, a plastic cover slide with an ~1.5mm hole is placed over the samples to retard evaporation, and a period of about 10 minutes is allowed for equilibration. The capillary tip is then inserted into a sample through the hole in the plastic disc, and after about 15 seconds the measurement is recorded. After each measurement, the tip is washed with distilled water and wiped before insertion into a new sample. When all samples in the adapter have been measured, the solutions are removed by inserting absorbent paper into the holes. Each hole is then washed with distilled water and blotted dry before refilling with a new sample. Alternatively, the sample or water wash can be removed with a section of fine plastic tubing attached to a vacuum source.

Results and discussion

Figure 2 presents a calibration curve for the 4-hole adapter with a series of chloride standards ranging in concentration from 0.01 to 0.00012 mole/liter. The sample size was 10 μl, but samples as small as 3 μl can be determined. The concentration range for linear response and the slope of the curve (59.0 mV/log Cl^- mole/liter) agree very well with the manufacturer's performance specifications for the chloride electrode used in the conventional manner for large sample sizes.

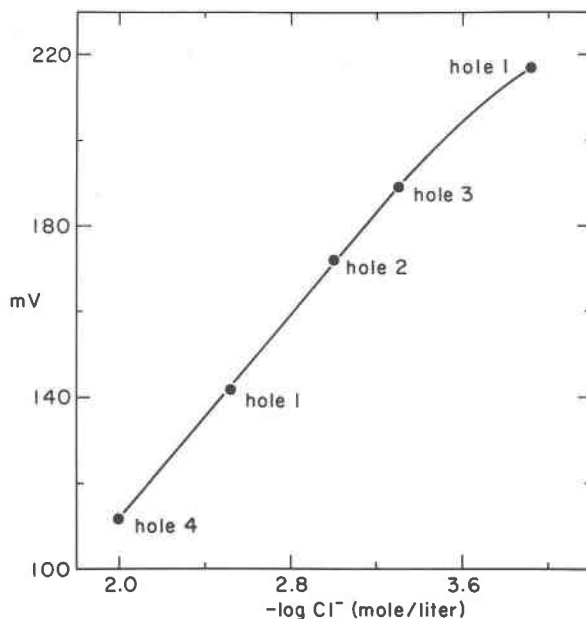A second series of calibration runs was carried out

Fig. 2. Results of calibration measurements for the chloride electrode with HCl standards.

in order to determine the scatter in measurement and to test for systematic differences between holes. The standard deviation for measurements with the same concentration in all four holes increased systematically from 0.5 mV at 10^{-2} mole/liter chloride to 1.9 mV at a chloride concentration of 1.2×10^{-4} mole/liter, which corresponds to a precision of 2% and 8% in the determination of chloride at these levels. In addition, small systematic differences on the order of 1 mV were found between the holes.

In addition to expanding the capability of the chloride electrode to microsample sizes, the system is rapid in that all four samples in the adapter approach a stable potential simultaneously.

Acknowledgments

References

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