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DETERMINATION OF PARTS-PER-MILLION CESIUM IN SIMULATED
NUCLEAR WASTE WITH THE CESIUM-SELECTIVE ELECTRODE

by

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BRIEF

A liquid-membrane electrode that contains cesium tetraphenylboron is described. For the application, cesium is first separated from high sodium concentrations by extraction with 4-sec-butyl-2(α-methylbenzyl)phenol.

ABSTRACT

A cesium-selective electrode with a liquid membrane of cesium tetraphenylboron dissolved in 4-ethylnitrobenzene gave near-Nernstian response (slope of 52 mV per decade) from 10^{-1} to $<10^{-4}$M Cs^+. Major interferences were NH_4^+, Ag^+, and Hg^{2+}. At 10^{-4}M Cs^+, the pH range was 6-8. For the application, cesium was first extracted from high sodium, strongly alkaline solutions with 1M 4-sec-butyl-2(α-methylbenzyl)phenol (BAMBP) in cyclohexane. Electrode measurements were then made in 0.01M Tris-HCl buffer solution at pH 7.1. By the standard addition method, cesium concentrations $\geq 5 \times 10^{-5}$M can be determined with relative standard deviation and relative bias <5%.

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Because of the simplicity of measurement, ion selective electrodes merit consideration when the concentration of a given ion in a set of solutions with similar compositions must be determined. Thus, the ion selective electrode technique was evaluated for determination of cesium in nonradioactive test solutions from our nuclear waste management program (1).

Electrodes that respond to cesium have been described. These include commercial potassium-selective electrodes that show a high selectivity for cesium (2) and that contain either a neutral carrier (e.g., valinomycin or a crown compound) or potassium tetra-p-chlorophenylboron. Of the cesium electrodes described in the literature, one is an electrode with a sensor of cesium 12-molybdophosphate in silicone rubber (3), and the other is a "liquid state" electrode that contains cesium tetraphenyl-boron (4).

None of these electrodes was suited to our present purpose. Although the potassium electrodes showed good initial response to cesium, they tended to drift after continued use in cesium solutions; also, the response to potassium is potentially troublesome. Of the two cesium electrodes, the molybdophosphate electrode was not sufficiently sensitive, and the reliability of the "liquid state" electrode for routine analyses was uncertain. Therefore a cesium-selective electrode of the proven liquid membrane type was developed.

This paper describes preparation and testing of a liquid membrane electrode that contains cesium tetraphenylboron dissolved in 4-ethylnitrobenzene. The electrode can determine cesium to $\sim 10^{-5}$M (1.3 ppm) and exhibits good selectivity for cesium over potassium and sodium. An extraction procedure with 4-sec-butyl-2(α-methylbenzyl)phenol (BAMBP) (5) was adapted to remove cesium from the highly salted, strongly alkaline test solutions, prior to determination of cesium with the electrode.

EXPERIMENTAL

Reagents

Deionized water and reagent-grade chemicals were used to prepare solutions of cesium and other salts.

4-ethylnitrobenzene (ENB), from Aldrich Chemical Co., was vacuum distilled before use.

Cesium tetraphenylboron (CsTPB) was prepared by precipitation from aqueous solution that contained excess CsCl. The filtered

product was dried either 1-2 hours at 115°C or 4-5 hours under vacuum over P_2O_5 at room temperature. The mode of drying did not affect the behavior of the product in the electrode. A saturated solution in ENB was prepared by stirring the CsTPB in warm ENB and filtering; the solution contained <1% CsTPB.

3M lithium trichloroacetate was prepared by neutralization of CCl_3COOH with LiOH and filtering; the pH of the solution was ∿6.

The BAMBP, $C_4H_9-C_6H_3(OH)-CH(CH_3)-C_6H_5$, synthesized on special order by Kennedy and Klim, Inc., Little Silver, NJ, was a light yellow liquid with a stated bp of 195 ±2°C (10 mm) and a refractive index of 1.5580 at 25°C. Titration of the material in pyridine solution by tetramethylammonium hydroxide in isopropyl alcohol, a procedure similar to that described by Egan et al. (6), indicated a purity of ∿90%. The BAMBP was used as received.

BAMBP solution for the extractions was made by diluting 50 ml BAMBP to 250 ml with cyclohexane (Fisher Certified).

Simulated waste solution (SWS) was prepared by the following procedure, which produced a clear, relatively stable solution. A solution of 0.50 moles of $Al(NO_3)_3 \cdot 9H_2O$ in 300 ml H_2O was slowly added, with stirring, to a solution of 2.75 moles of NaOH in 200 ml H_2O. Then the following solid reagents were added: 0.70 moles $NaNO_3$, 1.10 moles $NaNO_2$, 0.30 moles Na_2SO_4, and 0.30 moles Na_2CO_3. The solution was diluted to one liter.

Tris-hydroxymethylaminomethane (Tris) is a National Bureau of Standards Reference Material. The dilute Tris buffer used as supporting electrolyte in the cesium extraction tests was made by dilution of 50 ml 0.1M Tris and 40 ml 0.1M HCl to 500 ml with de-ionized water. The pH was 7.1.

Preparation of Electrode and Electrode Measurements

The cesium-selective electrode was assembled in the Orion Liquid Membrane Electrode Body, No. 920000, with Orion porous membranes soaked in petroleum ether and air-dried before use. The organic "exchanger" phase in the electrode was a saturated solution of CsTPB in ENB. The internal aqueous solution was 0.1M CsCl saturated with AgCl.

The criterion for satisfactory electrode fabrication is positive wicking of the organic through the membrane; the membrane should be transparent and show a slight wetting by the organic. After use in aqueous solution, the membrane may temporarily appear opaque, but it should recover its transparency during the customary storage upright in air.

The reference electrode was the Orion Double Junction Reference Electrode, No. 900200, with the outer chamber filled with 3M lithium trichloroacetate. This filling solution attacked the inner O-ring of the electrode, which made it necessary to replace the O-ring from time to time.

The potential measurements were made with an Orion Model 801 digital pH/mV meter or with a Beckman expanded-scale pH meter, at room temperature, $\sim$24°C. The solutions were stirred magnetically.

BAMBP Extraction of Cesium from SWS

All extractions were made by mixing the solutions for one minute on a Vortex mixer and centrifuging before withdrawal of the bottom (aqueous) layer by transfer pipet.

First 10 ml SWS, spiked with $CsNO_3$, was extracted with 10 ml BAMBP solution. Then the organic layer, which contained the cesium, was extracted with 0.3M NaOH. After the NaOH was withdrawn, the walls and sides of the tube were rinsed, without mixing with the BAMBP, with 5 ml H_2O, which was discarded. The cesium was then extracted from the organic phase with 1M HCl. The aqueous

phase was transferred quantitatively to a 50 ml beaker; after addition of 1 ml concentrated HNO_3 to decompose the entrained organic, the solution was evaporated to dryness. The residue was dissolved in 10 ml dilute Tris buffer for the electrode measurement.

When BAMBP was used more than once, it was necessary to wash the BAMBP thoroughly with water before reuse. Otherwise the residual acid in the BAMBP reacted with the nitrite of the SWS and degraded the BAMBP, which turned orange.

In the tracer study, the SWS was spiked with ^{137}Cs in addition to nonradioactive $CsNO_3$, and the above procedure was followed. The ^{137}Cs content was determined by gamma counting 5 ml (total) solution with a Ge(Li) detector.

RESULTS AND DISCUSSION

Response and Selectivity of Electrode

A typical calibration curve for the electrode in CsCl solution, Figure 1, shows that the response is linear above $10^{-4}M$ in the Nernst plot of potential versus logarithm of ion activity. In the absence of available values for Cs^+ activity, those tabulated for K^+ were used (7). The slope of the line is 52 mV per ten-fold change in Cs^+ activity. The calibration curve was made under optimum conditions, at neutral pH with no interfering ions present. Stable readings were obtained within 1-3 minutes.

The effect of pH is shown in Figure 2 for two different electrodes. The pH of the initial solution was altered by addition of small volumes of HCl or NaOH. At 0.1M Cs^+ there was no effect from pH 2.5 to 9.5. The useful pH range decreases at lower cesium concentrations, and at 10^{-4}M Cs^+, the range is 6-8. No appreciable difference in response between the two electrodes was observed.

Selectivity of the electrode for cesium, relative to other cations, was determined as previously described (8) from measured potentials (E_{Cs} and E_M) in separate 0.1M CsCl and 0.1M MCl_z solutions. The selectivity constant, K_{CsM}, was calculated with average single ion activities, a_M, using the equation:

$$\log K_{CsM} = \frac{(E_M - E_{Cs})}{52} + \log (a_{Cs}/a_M^{1/z}) \tag{1}$$

Selectivity constants are presented in Table I. Major interferences are Ag^+, $(CH_3)_4N^+$, and Hg^{2+}. The footnote shows that selectivity of this electrode for cesium over potassium is considerably better than that of the Beckman or the Orion potassium electrode, which use a neutral carrier; selectivity is slightly better than that given for the Corning potassium electrode, which contains potassium tetra-p-chlorophenylboron.

Chloride and nitrate, the only anions used in the investigation, do not interfere, and interference from other common anions is not anticipated.

To supplement the selectivity values that were determined at 0.1M concentrations, the effect of lower background concentrations of Na^+, K^+, H^+, and Tris-HCl on electrode response was determined. Figure 3 shows the change in the potential reading in the presence and absence of background solute at various cesium concentrations. The presence of $10^{-4}M$ KNO_3 or $10^{-3}M$ $NaNO_3$ does not affect electrode response even at $10^{-5}M$ Cs^+. Dilute Tris buffer causes a negative bias, which gradually diminishes as the cesium concentration increases; this has the effect of increasing sensitivity slightly at low Cs^+ concentrations. Similar behavior in $10^{-2}M$ NaOH and $10^{-2}M$ $NaNO_3$ probably reflects response to sodium ion rather than to pH. The effect of HNO_3 is greater than that observed with HCl in the pH study (Figure 2).

Determination of Cesium in SWS

The electrode could not be used directly in the strongly alkaline solutions of high sodium content, typified by SWS. Therefore cesium was separated for the determination by solvent extraction with BAMBP (5). This procedure eliminated the sodium interference, and the final solution of neutral pH and consistent ionic strength was well suited to ion-selective electrode measurement. The effectiveness of the BAMBP extraction was established by supplementary experiments: a ^{137}Cs tracer study and miscellaneous analyses of extraction solutions by atomic absorption/emission spectrometry.

Results of the tracer study, in which ^{137}Cs was spiked into SWS that contained $10^{-4}M$ $CsNO_3$, are given in Table II. The extraction was 98% efficient; however, recovery of the ^{137}Cs was only 95%. The reason for the loss of the tracer is not known. Volume changes of the various phases were too small to cause an apparently low cesium recovery.

Analyses by atomic emission spectrometry showed >95% recovery of 10^{-4} and $10^{-5}M$ Cs^+ in SWS by the extraction procedure. The fate of Na^+ and K^+ (a contaminant of the sodium salts in SWS) was determined by atomic absorption spectrometry. The results in Table III show that the Na^+ is reduced to tolerable levels by the 0.3M NaOH wash and that the potassium is not carried with the cesium.

BAMBP extractions and cesium determinations with the electrode were made at cesium concentrations $<4 \times 10^{-4}M$ in SWS, the region of interest. Calibration curves were made by adding $CsNO_3$ to dilute Tris buffer solution. The precision and accuracy were not improved when blank extractions were spiked with cesium to establish the calibration. The residual salts after the BAMBP extraction procedure did not interfere with the electrode response, except perhaps at $10^{-5}M$, where the sensitivity of the electrode was already marginal

Table IV presents the cesium concentrations found from several measurements with one cesium electrode. The standard

deviation of the measured potentials is included. Precision improves as the concentration increases. For this set of measurements the measured potential at 10^{-5}M was less than the potential of the calibration point at 10^{-5}M, and consequently no estimate of measured cesium could be made. The result was included to illustrate uncertainties encountered at this low concentration.

Table V shows cesium concentrations averaged from replicate measurements with two or more electrodes. The effect of reusing the BAMBP extractant is also shown and appears negligible at the higher concentrations. At the lower concentrations, close inspection of the data suggest that high results occur, perhaps because of carryover of Na^+ to interfering levels.

The direct method described above, in which the measured potential of a sample solution is compared with a calibration curve, is generally less precise and more subject to error than a differential method. Therefore the standard addition method (9) was also demonstrated. The electrode response was assumed to be linear with the observed slope of 52 mV per decade of concentration in the range 5×10^{-5} to 4×10^{-4}M Cs, based on average least square values from electrode calibrations in dilute Tris buffer. The slope obtained from calibrations in blank extraction solutions was somewhat less and gave calculated cesium concentrations that were too low. The concentration of cesium in the sample (c_{Cs}) is calculated from the increase in potential (ΔE) observed

when standard Cs^+ (x_n) is added, by the equation

$$c_{Cs} = \frac{x_n}{\left[\log^{-1}\left(\frac{\Delta E}{52}\right)\right] - 1} \qquad (2)$$

when the Nernst relationship is applied with a slope of 52.
For analyses of three representative solutions in Table VI,
agreement between the known cesium content and that determined
by the standard addition method is satisfactory; agreement is
improved at higher concentrations. Although these results suggest
the precision is extremely good, a relative standard deviation
of 2-5% is more realistic. The method is limited to concentra-
tions $\geq 5 \times 10^{-5}$M because of the linear response required.

Variation of the extraction procedure to accommodate larger
volumes of SWS is limited by the requirement that the final
sodium concentration be maintained below the interference level
for the electrode. The volume of BAMBP (10 ml) used in the
extraction is linked to the final aqueous volume (10 ml), which
is the minimum suitable for measurement with the present electrode
system. The 10 ml of BAMBP could be used to extract larger
aqueous volumes, either singly or serially, but use of signifi-
cantly larger volumes of BAMBP could increase the sodium concen-
tration to interfering levels.

The procedure was explored for low concentrations of cesium
because this was the area of interest. The results reflect the
fact that many measurements were near the limit of the electrode

sensitivity. With higher cesium concentrations, where cesium electrode response is more certain and less subject to interferences, precision and accuracy, particularly for direct measurements, should improve.

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TABLE I

Selectivity Constants for the Cesium-Selective Electrode

(0.1M MCl_z Solutions)

M^{z+}	K_{CsM}
$(CH_3)_4N^+$	9×10^1
Ag^+	2×10^1
Cs^+	1×10^0
K^+	3×10^{-2} [a]
NH_4^+	6×10^{-3}
H^+	1×10^{-3}
Na^+	4×10^{-4}
Li^+	2×10^{-4}
Hg^{2+}	3×10^{-1}
Co^{2+}	3×10^{-4}
Cu^{2+}	2×10^{-4}
Ca^{2+}	8×10^{-5}
Mn^{2+}	6×10^{-5}
Ba^{2+}	6×10^{-5}
Sr^{2+}	6×10^{-5}
Ni^{2+}	4×10^{-5}
Mg^{2+}	3×10^{-5}
Zn^{2+}	3×10^{-5}
Al^{3+}	1×10^{-4}

a. For comparison, K_{CsK} values for commercial potassium-selective electrodes are: Beckman, 2.0; Orion, 1.0; Corning, 0.05 (2).

TABLE II

^{137}Cs Tracer Study of BAMBP Extraction

^{137}Cs, counts/(min)(ml)

Original Aqueous:
   SWS + 10^{-4}M CsNO$_3$ + ^{137}Cs.   22,054

1st Extraction:
   Aqueous phase after BAMBP extraction
   of original aqueous   318

2nd Extraction:
   Aqueous phase after 0.3M NaOH extraction
   of BAMBP from 1st extraction   171

3rd Extraction:
   Aqueous phase after 0.1M HCl extraction
   of BAMBP from 2nd extraction   20,388

Organic phase (BAMBP) after 3rd extraction   9

TABLE III

Behavior of Sodium and Potassium in BAMBP Extractions

Solution	Concentration, M^a	
	Na^+	K^+
Original SWS	6	1×10^{-4}
Extracted from SWS by BAMBP[b]	0.05	2×10^{-5}
In BAMBP after SWS extraction followed by 0.3M NaOH extraction[b]	0.001	6×10^{-6}

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a. SWS Na^+ concentration from composition of solution; other concentrations from analyses by atomic absorption spectrometry.

b. Back-extracted from BAMBP into 1M HCl prior to analysis.

TABLE IV

Extracted Cs Determined from Measurements with One Cs Electrode

Determinations	Measured Potential, mV		Cs Concentration, M		RSD, %	Bias, %
	Average	σ	Added	Found		
3	-155.8	1.8	0	-	-	-
5	-151.8	1.4	1×10^{-5}	$<10^{-5}$	-	-
5	-131.9	0.9	5×10^{-5}	5.5×10^{-5}	4	+10
4	-120.4	0.6	1×10^{-4}	9.6×10^{-5}	4	- 4

TABLE V

Effect of Repeated Use of BAMBP Extractant

Cs Added, M	Cs Found[a] First Use M	RSD, %	Bias, %	Second Use M	RSD, %	Bias, %	Third Use M	RSD, %	Bias, %
1×10^{-5}	-	-	-	2.1×10^{-5}	46	+110	1.61×10^{-5}	31	+60
5×10^{-5}	5.2×10^{-5}	21	+4	5.5×10^{-5}	21	+10	6.6×10^{-5}	15	+32
1×10^{-4}	1.09×10^{-4}	8	+10	1.01×10^{-4}	12	+10	9.6×10^{-5}	13	-4
2×10^{-4}	1.97×10^{-4}	5	-3	1.98×10^{-4}	13	-1	2.0×10^{-4}	8	+1
4×10^{-4}	3.9×10^{-4}	5	-3	-	-	-	-	-	-

a. Average of repetitive measurements by 2 or more electrodes.

TABLE VI

Determination of Cs Concentration in BAMBP Extraction
By Standard Addition Method

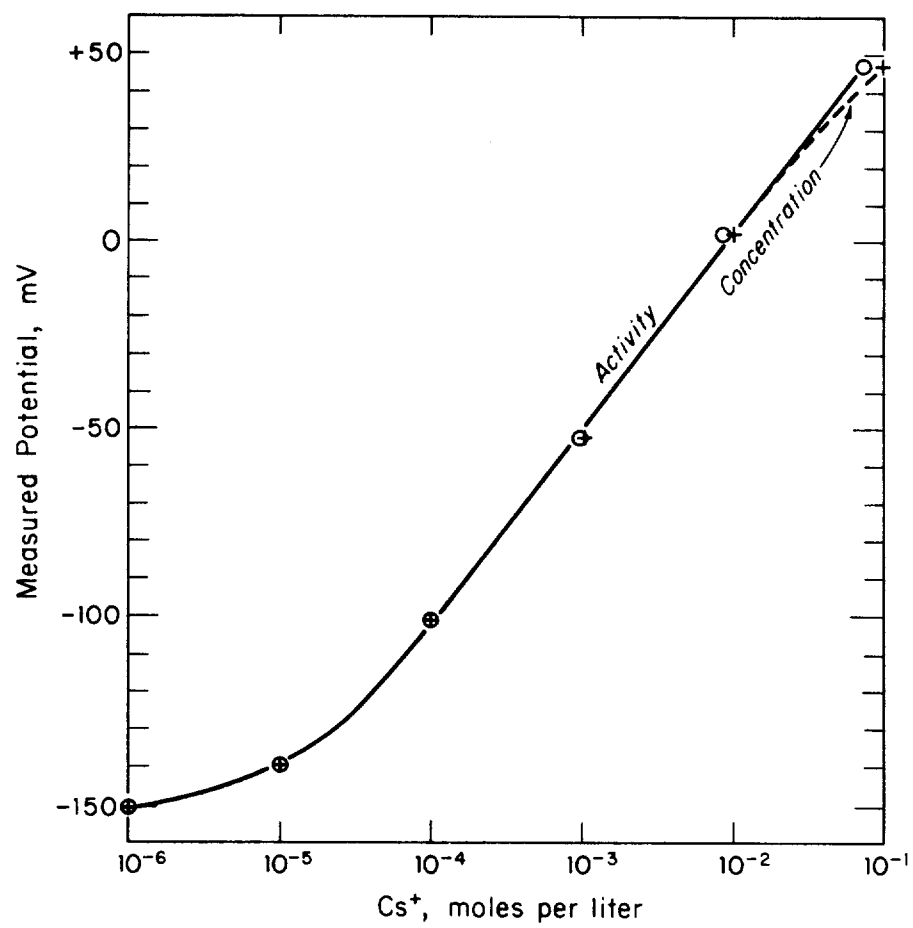| Known Initial Cs	Added Cs (x_n), M	ΔE (mV)	Calculated Initial Cs (c_{Cs})
5.0×10^{-5}	5×10^{-5}	15.5	5.1×10^{-5}
	1×10^{-4}	24.5	5.1×10^{-5}
	1.5×10^{-4}	31.0	5.1×10^{-5}
8.0×10^{-5}	4×10^{-5}	8.8	8.3×10^{-5}
	9×10^{-4}	16.8	8.2×10^{-5}
	1.4×10^{-4}	22.7	8.1×10^{-5}
1×10^{-4}	5×10^{-5}	9.3	0.98×10^{-4}
	1×10^{-4}	15.8	0.99×10^{-4}

LIST OF FIGURES

Figure 1.   Response of Cs-Selective Electrode
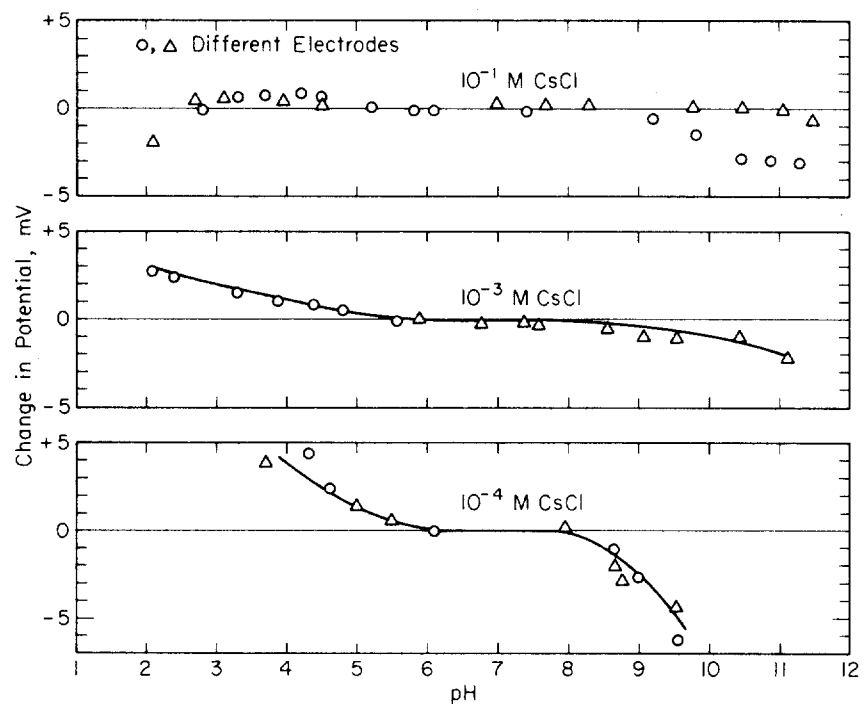in CsCl Solutions

Figure 2. Effect of pH on Potential
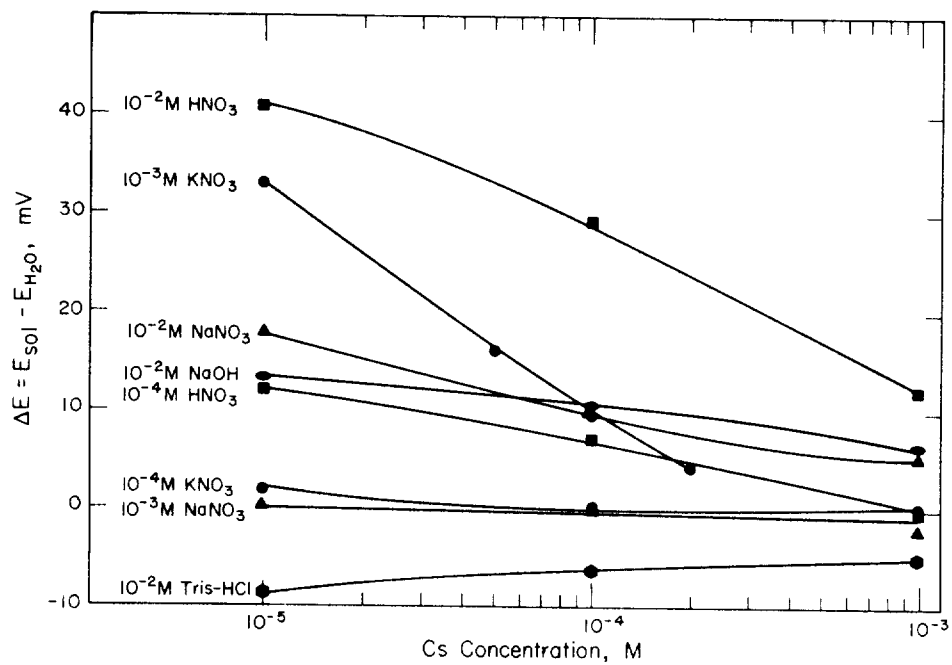of Cs-Selective Electrode

Figure 3.   Effect of Various Solutes on Potential
of Cs-Selective Electrode