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Hydroxide Ion-Selective Polymeric Membrane-Coated Wire Electrode Based on Oxomolybdenum(V) Tetraphenylporphyrin Complex

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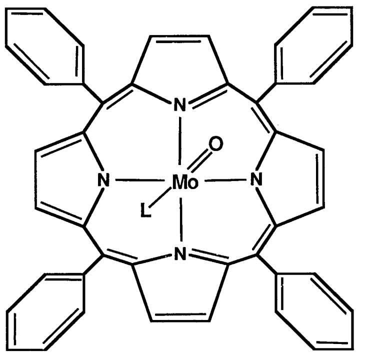
A coated wire electrode (CWE) was prepared by use of a poly(vinyl chloride)-supported liquid membrane containing oxoethoxo(5,10,15,20-tetraphenylporphyrinato)molybdenum(V) as a carrier. CWE based on such a metallo-porphyrin complex exhibits near-Nernstian responses to varying concentrations of NaOH, NaF, and C_2H_5OH, especially to NaOH over a wide concentration range. The pOH response curve was influenced by certain anions other than OH^- ion, but not by cations such as Li^+, Na^+, K^+, and Cs^+. The mixed solution method gave a selectivity sequence $OH^- \gg ClO_4^- > NO_2^- > F^- \sim SCN^- > I^- > NO_3^- > SO_3^- > Br^- > SO_4^{2-}$, with a preference for OH^- over ClO_4^- by $10^{4.6}$ and over F^- (or SCN^-) by $10^{6.2}$. In addition, Cl^- ion was found to have little interfering effect under conditions used in the measurements of selectivity coefficients. Both response-time profile and pOH-response curve scarcely varied even when CWE was stored in distilled water for 167 days.

At present there are several reports on anion-selective liquid membrane electrodes based on metallo-porphyrin complexes; i.e., tetraphenylporphyrin complexes of cobalt(III),[1] manganese(III),[2] and tin(IV).[3] Before the publications of these studies, a lipophilic derivative of vitamin B_{12} having a structure similar to Co(III)-porphyrins was employed for developing a nitrite-selective polymeric membrane electrode.[4–6] Evidence has since then accrued which indicates that electrodes based on such porphyrin or porphyrin-like carriers differ from those based on classical ion exchanger in the selectivity pattern with respect to various anions. This is because the complex carrier in the electrode membrane interacts with specific anion in the aqueous phase. In cases of classical ion exchangers, however, the selectivity is governed only by the free energy of transfer of anions from the aqueous to the membrane phase. Thus, applications of metallo-porphyrin complexes to anion-selective electrodes will serve to enhance and/or improve their selectivities against the anion to be measured.

Oxo(5,10,15,20-tetraphenylporphyrinato)molybdenum(V), MoO(L)TPP, has a structure in which the 6th coordination position of Mo(V) atom is occupied by various ligands (L): OH^-, $C_2H_5O^-$(EtO^-), F^-, NCO^-, and so on. The electronegativity of the axial ligands affects the nature of the complex,[7,8] which has been elucidated by UV/visible spectroscopy because the spectral changes are dependent on the magnitude of donating electrons from a ligand to the porphyrin ring via the central metal atom. In particular, hydroxide ion was found to be one of the ligands causing dramatic changes in the spectrum when it was measured in CH_2Cl_2.[8] This prompted us to apply MoO(L)TPP to a hydroxide ion-selective polymeric membrane electrode.

The purpose of the present work is to prepare a coated wire electrode (CWE) using a MoO(L)TPP-containing liquid membrane supported by poly(vinyl chloride) (PVC) and to examine its OH^--selectivity in the presence of several common anions.



MoO(L)TPP

Experimental

Materials. Oxoethoxo(5,10,15,20-tetraphenylporphyrinato)molybdenum(V), MoO(EtO)TPP, was the same samples as used in our previous works concerning a selective phosphate-ion exchanger[9] and uphill transport of dihydrogenphosphate ion.[10,11] PVC (weight-average molecular weight of 6.88×10^4) was commercially obtained from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Dioctyl adipate (DOA) as a plasticizer was also of commercial origin (Tokyo Kasei Kogyo Co., Japan). All other reagents were of analytical grade and obtained from commercial sources. Distilled and subsequently deionized carbonate-free water was used throughout.

Preparation of CWE. A silver wire (1.5 mm diameter; 70 mm height) was covered with a plastic tube, so as to leave both ends with 10 mm of length. One of the ends was chloridized, then coated with a PVC-supported liquid membrane composed of 66% (w/w) DOA, 33% (w/w) PVC, and 1% (w/w) MoO(EtO)TPP. The membrane was formed by dip-coating method; repetition (10 times) of both soaking (1 min) and air-drying (60 min) procedures using a tetrahydrofuran solution of the materials. The resulting CWE was thoroughly air-dried, soaked in an aqueous ethanol solution (1 M; M=mol dm^{-3}) to secure a ethoxide form of the complex

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in the membrane phase, and finally air-dried for 2 or 3 days. The electrode membrane prepared has a thickness of 400 μm and a direct current resistance of 22 MΩ, as determined by the same manner as reported previously.[12]

Measurements of Electromotive Force (EMF). Cell assemblies in the measurements were as follows: Ag/AgCl| membrane| sample solution|| KCl(saturated)| Hg_2Cl_2/Hg. The EMF values were determined at 25±1 °C in a nitrogen atmosphere using an Ion Meter IOC-10 (Denki Kagaku Keiki Co., Japan). The sample solution was magnetically stirred in a double-wall glass container connected with a circulating bath. The electrode system and millivolt meter were kept in a grounded wire-net cage to cut off any electrical noise. The experimental EMF values were corrected for the changes of the liquid-junction potential between the external reference electrode and a sample solution, which was computed according to the Henderson equation.[13]

Measurement of pH. The pH measurements were carried out at 25±1 °C in a nitrogen atmosphere using a Denki Kagaku Keiki MG-7 pH-meter. A combination pH electrode (Denki Kagaku Keiki, model 6155) consisting glass and Ag/AgCl reference electrodes incorporated in single stem was employed after a calibration at 25 °C with standard buffers of pH 4.01, 6.86, and 10.02.

Selectivity Coefficients. The evaluation of the selectivity was made by the mixed solution method which has been recommended by IUPAC.[14] The concentrations of various interfering ions were fixed at 0.01 M throughout all the measurements. The pH values of the sample solutions were carefully adjusted with a NaOH/HCl system.

Results and Discussion

Calibration Curves for NaOH, Ethanol, and NaF. The CWE based on MoO(EtO)TPP was first characterized by studying its EMF responses to varying concentrations of NaOH, C_2H_5OH, and NaF. These solutes were selected because of possible formation of anion ligands in an aqueous medium which have very high binding affinity toward the carrier complex used. The results obtained are shown in Fig. 1, together with that of a control experiment performed by using NaOH solutions and a carrier-free CWE. In contrast to the carrier-free electrode, all the calibration curves for the complex-based CWE give linear plots in certain concentration range of each solute. The slope of each straight line was within −54 to −58 mV/log [solute], indicating that the electrode exhibits near-Nernstian responses to varying concentrations of all the solutes examined.

Comparison of the calibration curves in Fig. 1 evidenced that NaOH obviously brings about a better result than the other solutes in EMF response of CWE. This may reflect a strong interaction of the complex carrier in the electrode membrane with OH^- ion in the aqueous phase. Thus, the present work mainly assesses the performance of CWE with respect to OH^--selective sensing.

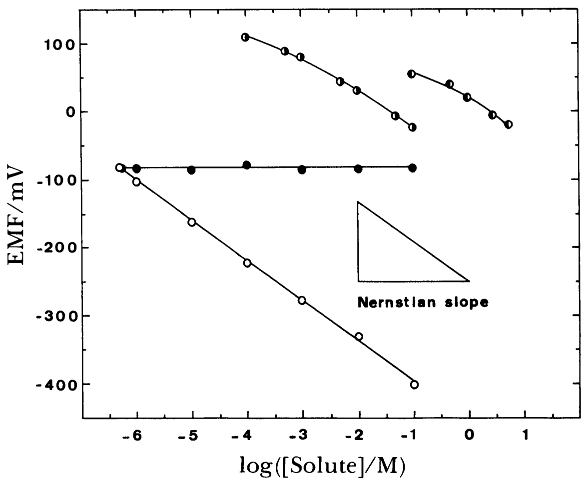

Fig. 1. Responses of CWE based on MoO(EtO)TPP in aqueous solutions containing NaOH (○), NaF (◑), and ethanol (◐). A control experiment (●) was made by measuring EMF under different concentrations of NaOH using a carrier-free CWE having a membrane composition of 67% (w/w) DOA and 33% (w/w) PVC. All the measurements were done after adjusting the initial EMF value to 0 mV by distilled water.

Hodinár and Jyo have pointed out in their work on a Co(III)-tetraphenylporphyrin-based thiocyanate-selective membrane electrode that adequate selection of a counter ion of the carrier complex was advantageous for increasing SCN^--selectivity.[1] Taking this into account, we prepared three samples of the MoO(L)-TPP complex (L=OH^-, F^-, and Cl^-) other than MoO(EtO)TPP according to the literature,[8] and applied to CWE studies. However, such a conversion of the anion ligands did not give a marked effect on the selectivity of CWE against various anions when evaluated in the same manner, as described in the sections below. Consequently, only results from CWE based on MoO(EtO)TPP were reported in detail.

pOH Response in the Presence of Several Anions. In order to clarify that the potentiometric response of CWE to NaOH is due to OH^- but not to Na^+ (or H^+), the EMF measurements in aqueous solutions at pOH 1 to 13 were carried out in the presence of a fixed amount of NaCl, $NaNO_3$ or $NaClO_4$. The pOH values of the sample solutions were determined from their pH values according to a relationship of pOH = 13.996 −pH (25 °C). As can be seen from Fig. 2, the slope of EMF vs. pOH curve in the presence of $NaNO_3$ or $NaClO_4$ decreases when pOH goes up to a certain value. In addition, the magnitude of such a decrease in the slope varies depending on the species of anions. These results are consistent with the general phenomena relating to interfering effects of common anions on the EMF response of an anion-selective electrode. Thus, it can be said that the complex-based CWE responds to anions, especially to OH^-.

Effect of Cations on the pOH Response. To gain further insight regarding the pOH response of CWE,

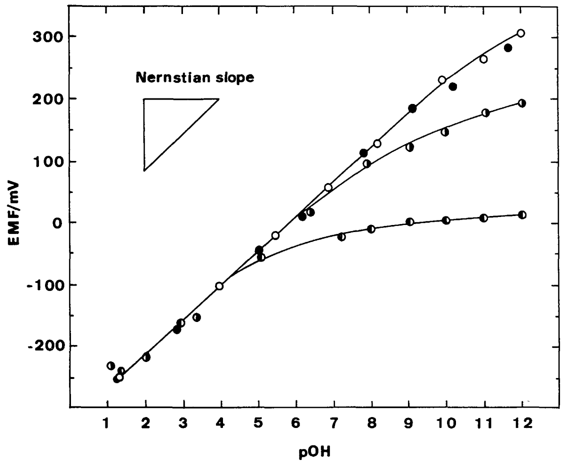

Fig. 2. Responses of MoO(EtO)TPP-based CWE to pOH in the absence (○) and presence of NaCl (●), NaNO$_3$ (◑), or NaClO$_4$ (◐). The pOH values of the sample solutions containing 0.01 M of each salt were adjusted with NaOH (4 M) or acids (6 M) composed of the corresponding anions. All the measurements were made after adjusting the initial EMF value to −100 mV by a standard NaOH solution of pOH 4.00.

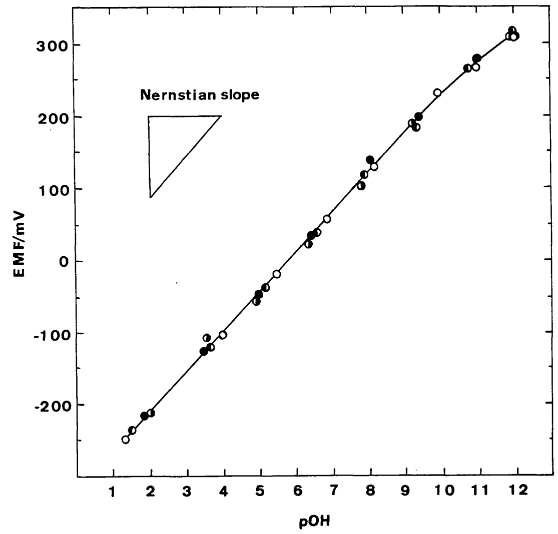

Fig. 3. Responses of MoO(EtO)TPP-based CWE to pOH in the absence (○) and presence (0.01 M) of LiCl (●), KCl (◑), or CsCl (◐). The initial EMF was adjusted to −100 mV in the same manner as described in Fig. 2.

effects of various metal cations were examined. Chloride salts of the corresponding cations were employed in this experiment, because Cl$^-$ was found to be little or no interfering effect on the pOH response (see previous section). The results obtained were shown in Fig. 3. No distinguishable difference was observed between the EMF vs. pOH curves in the absence and presence of all the cations studied. As a result, it has became apparent that CWE responds to anions but not to cations.

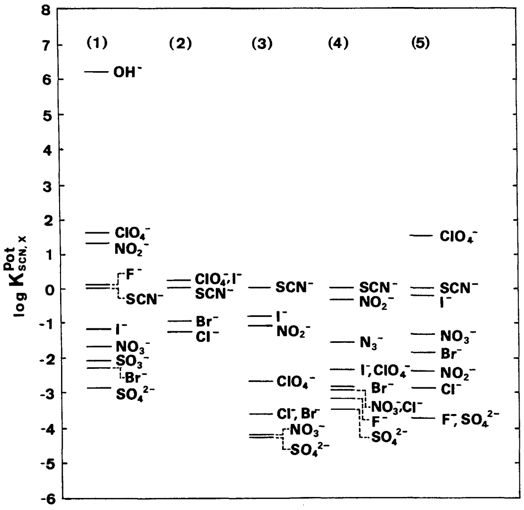

Fig. 4. Comparison of the selectivity coefficients $K^{Pot}_{SCN,X}$ for MoO(EtO)TPP-based CWE (1) and the other electrodes based on Mn(Cl)TPP (2), Co-(SCN)TPP (3), vitamin B$_{12}$ (4), and MTDDACl (5). The present data (first column) were determined by the mixed solution method, while the others (second to fifth columns) cited from the references in the text were obtained according to the separate solution method.

Selectivity of CWE. The selectivity of MoO(EtO)-TPP-based CWE was investigated by the mixed solution method. The results obtained are summarized in Fig. 4, together with those of the previously reported anion-selective electrodes based on the tetraphenylporphyrin complexes of Co(III)[1] and Mn-(III)[2] and also on vitamin B$_{12}$.[4] In addition, Fig. 4 includes an anion-selectivity sequence of an electrode based on methyltridodecylammonium chloride (MTDDACl) as a typical anion exchanger.[15] In the studies cited here, the selectivity coefficient relative to Cl$^-$ ion was used for evaluating anion selectivities of the electrode membranes. In this study, however, the selectivity coefficient ($K^{Pot}_{SCN,X}$) in relation to SCN$^-$ was employed as a matter of convenience, because the interfering effect of Cl$^-$ on pOH response was negligible (see Fig. 2). For the sake of comparison with our results the previous date were also converted into $K^{Pot}_{SCN,X}$ by recalculation (see Fig. 4).

First, it was found from Fig. 4 that the CWE based on MoO(EtO)TPP exhibits a rather high selectivity against OH$^-$ ion. The detection limit for OH$^-$ in 10^{-3} M solutions of various interfering anions is as follows: $>10^{-7.7}$ M for ClO$_4^-$ and NO$_2^-$; $>10^{-9.2}$ M for F$^-$ and SCN$^-$; $>10^{-10.4}$ M for the others. A comparison of the present and previous results regarding OH$^-$-selectivity seems to be available for evaluating the capability of MoO(EtO)TPP as the carrier in the OH$^-$ ion-selective electrode membrane. However, we are forced to abandon this idea from lack of selectivity data for OH$^-$ in the previous papers.[1,2,4]

Table 1. Comparison of the $K^{\mathrm{Pot}}_{\mathrm{SCN,X}}$ Values of the Electrodes Based on MoO(EtO)TPP and MTDDACl with Hydration Energy of Halide Ions and Stability Constants of Halo-complexes of MoO(L)TPP

Halide ions	$K^{\mathrm{Pot}}_{\mathrm{SCN,X}}$		Hydration energy/kJ mol^{-1}	Stability constant[a]
	MoO(EtO)TPP	MTDDACl		
I^-	−1.2	−0.25	38.0	5.20
Br^-	−2.3	−1.88	39.9	5.58
Cl^-	s[b]	−2.88	41.4	6.61
F^-	0.1	−3.75	49.3	l[c]

a) Cited from Ref. 10 in which the data were obtained by extracting a CH_2Cl_2 solution of the complex with an aqueous solution containing halide ion. b) Can not be determined because of a very small value (see Fig. 2). c) Can not determined because of a very large value (see Ref. 10).

Since it was not possible to directly compare the selectivity coefficients for OH^- in the present and previous papers, we compared the anion-selectivity sequences of each electrode shown in Fig. 4. Large differences in the selectivity sequences were observed depending on the species of the carriers applied into anion-selective electrodes. It has been pointed out that the selectivity coefficient obtained by the mixed solution method was not in accord with that by the separate solution method.[4] Even when such a result is taken into account, however, there are considerable differences in the selectivity sequence between the electrodes based on MoO(EtO)TPP and on the other porphyrin or porphyrin-like complexes. A difference in the $K^{\mathrm{Pot}}_{\mathrm{SCN,X}}$ values is also observed when comparing the present CWE with the MTDDACl-based electrode. These two results would suggest that the selectivity of CWE to anions, especially to OH^-, is closely associated with an interaction of the MoO(EtO)TPP carrier in the electrde membrane with the anion in the aqueous solution. In the cases of porphyrin or porphyrin-like complexes, moreover, the degree of such an interaction appears to vary depending on the species of the central metals.

To clarify further the role of the MoO(EtO)TPP complex in the observed anion-selectivity of CWE, the $K^{\mathrm{Pot}}_{\mathrm{SCN,X}}$ values for halide ions were compared with the stability constants of MoO(L)TPP (L= F^-, Cl^-, Br^-; and I^-) in a H_2O/CH_2Cl_2 system and also with the hydration energy of halide ions (see Table 1). Included in Table 1 for comparison are the selectivity coefficients of the MTDDACl-based electrode for halide ions. In the latter case, a decrease in the $K^{\mathrm{Pot}}_{\mathrm{SCN,X}}$ value with increasing the hydration energy is observed, which can be explained on the basis of the so-called Hofmeister lyotropic series. In contrast, the change in the $K^{\mathrm{Pot}}_{\mathrm{SCN,X}}$ value of the complex-based CWE can not be interpreted in the same way. A detailed comparison of the $K^{\mathrm{Pot}}_{\mathrm{SCN,X}}$ value with the stability constant, though a good correlation can not be obtained, indicates that CWE exhibits very high selectivity against F^- ion bringing about the most large stability constant. It is thus likely that the binding affinity of anions toward the carrier complex plays an important role in the anion-selectivity of the present electrode system. The lack of a correlation between the selectivity and stability data seems to be due to a difference in the organic solvent systems utilized in the preparation of the electrode membrane and in the determination of the stability constant. Organic solvent-induced alteration of the stability constant of MoO(L)TPP has been observed in our previous study,[11] in which the stability constants were measured by extraction experiments using different aqueous/organic systems.

Another remarkable feature of Fig. 4 is that the MoO(EtO)TPP-based CWE shows the selectivity with

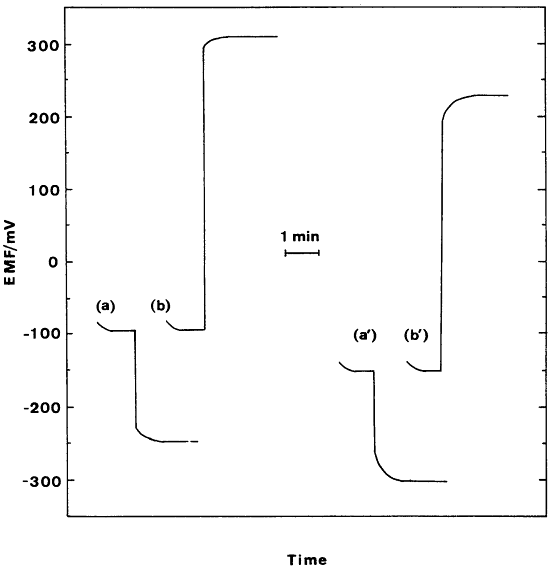

Fig. 5. Typical EMF–time profiles near pOH 1 and 12 for MoO(EtO)TPP-based CWE before (a and b) and after (a′ and b′) storage for 144 days in distilled water. The pOH values of the salt-free sample solutions were adjusted by use of 4M NaOH or 6M HCl to: 1.30 (a); 1.35 (a′); 12.01 (b); 11.67 (b′). All the curves recorded show a change in EMF before and after a quick replacement of the standard solution (pOH 4.0) by the sample solutions described above. The initial EMF of the newly prepared CWE was adjusted to −100 mV in the same manner as described in Fig. 2, while in the case of the stored CWE such a adjustment was not made in order to examine a shift in EMF during the storage.

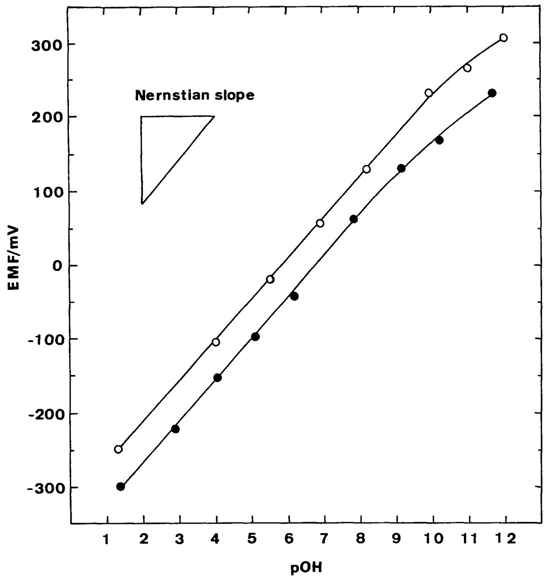

Fig. 6. pOH Response of MoO(EtO)TPP-based CWE before (○) and after (●) storage for 114 days. The technique for the EMF measurements was described in detail in Fig. 5.

a preference for NO_2^- over SCN^- (or F^-) and NO_3^- by $\geq 10^{1.3}$ and $10^{3.0}$, respectively. Thus, the present CWE would serve as a nitrite-selective electrode if we can choose an appropriate measuring condition.

Change in the pOH Response during Long-Term Storage. A newly prepared CWE was stored in distilled water at room temperature for about five months. The EMF response of this electrode was measured at fixed time interval (25 days). Figure 5 depicts the EMF-time profile after the storage. Sable EMF readings were attained very rapidly even after storage for prolonged times, and in each measurement the response time was within 60 s. On the other hand, a shifting of the calibration curve was observed during storage (see Fig. 6). There was no observable difference in the slopes of the calibration curves before and after storage.

Ledon et al. have studies solvent effects on monomer/dimer equilibrium of the hydroxo complex, MoO(OH)TPP, and demonstrated that the μ-oxo dimer complex, O=Mo(TPP)-O-(TPP)Mo=O, was preferentially formed in aromatic solvents such as benzene.[8] If such a dimer structure is produced in the electrode membrane when coming into contact with an aqueous solution including OH^-, the EMF response of CWE would be altered during storage. However, no marked difference was observed in the pOH responses before and after storage. Thus, it appears more likely that the formation of the μ-oxo dimer from OH^--coordinated carrier complex does not take place in the present electrode system. This was confirmed by a qualitative spectroscopy for a PVC-supported liquid membrane having the same composition as used for the electrode.[16]

In conclusion, it has become apparent that a hydroxide ion-selective CWE can be prepared by use of the polymer-supported liquid membrane containing MoO(EtO)TPP as the carrier. In addition, the performance of the CWE prepared here remains unaltered during storage at least for 4 to 5 months.

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16) The membrane sample was prepared by casting on a quartz plate, followed by soaking in an aqueous NaOH solution (pH 12) for 10 h. The spectroscopic measurements were made with a Hitachi model 557 spectrophotometer.