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CATION EXCHANGE CAPACITY OF SUSPENDED MATERIAL FROM COASTAL SEA WATER OFF CENTRAL CALIFORNIA

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ABSTRACT

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The cation exchange capacity (CEC) of suspended particles (> 0.5 μ) in sea water is measured by a described methylene blue (MB) absorption method which has the following characteristics:

sample volume: minimum of 100 ml sea water;
time of measurement: about 10 min;
useful range: 0.1–10.0 μe/ℓ;
precision: ± 0.05 μe/ℓ at 0.7 μe/ℓ;
accuracy: function of organics and clay types.

Test of the MB method with sea water samples from the central California off-shore show background values of about 1 μe/ℓ with higher values up to 5 μe/ℓ in the vicinity of stream discharge.

INTRODUCTION

Sea water, in addition to chemical constituents and living organisms, contains a variety of both inorganic and organic suspended material (Harvey, 1963, p. 9). There is no natural or easily recognized lower size limit for suspended matter in sea water, so the particle size has been defined as: (1) suspended, particles > 0.5 μ and (2) dissolved, that which passes a 0.5 μ filter (Riley, 1965, p. 394). Most of the suspended particles have a charged surface and thus can enter into ion exchange reactions. The following develops a colorometric method by which the cation exchange capacity (CEC) of suspended matter in sea water can be determined rapidly.

CONVENTIONAL CEC MEASUREMENTS

Several techniques, such as ammonium acetate exchange (Bower et al., 1952, p. 251–261), Versenate (Perkins, 1952), and conductivity (Mortland and Mellor, 1954), have been used to estimate the CEC of many substances. The ammonium acetate method requires at least 50 mg of exchangeable material or 4 g of fine-textured soils (Richards, 1954, p. 101). Parsons (1963, p. 220) noted an average of 0.8–2.5 mg/ℓ total suspended matter containing 20–60% organic matter are found in open ocean water. Accordingly, the ammonium acetate method would require filtration of an average of 60–20 l of sea water to obtain the CEC of suspended matter. The problems associated with collecting and filtering such a large amount of sea water make the ammonium acetate method impractical for any systematic study of the CEC of suspended matter in sea water.

The Versenate method is dependent upon the saturation of the clay fraction with calcium or magnesium ions and their subsequent displacement with excess EDTA and its back titration with magnesium. A one gram sample is required, thus rendering this method impractical as with the ammonium acetate method.

The conductometric titration method is dependent upon the low solubility of barium sulfate. The clay fraction is saturated with barium ions and is titrated with sulfate. The procedure requires in excess of four hours to perform. Thus, this method is also impractical for sea water use.

PREVIOUS WORK ON THE METHYLENE BLUE METHOD

Adsorption of methylene blue by organics and clays

In the nearshore marine environment a significant number of organic particles are clay-organics and humus washed into the ocean by land-surface run-off. Soil humus has a CEC of 30–280 mequiv. per 100 g humus (Olson and Bray, 1938, p. 483) which, according to Hallsworth and Wilkinson (1958, p. 1), varies with pH or 70 mequiv. per 100 g humus at pH 4.8 to 300 mequiv. per 100 g humus at pH 7.2. However, Russell (1961, p. 282) feels there is no universally acceptable method by which the CEC of humus can be examined, because one cannot separate all the humus from the associated mineral soil without causing some chemical alteration of the original material, although he (p. 287) states the clay-humus complex may have a CEC a little less than that of the clay and humus if measured separately.

The chief difficulty in the interpretation of the CEC of mixed organics as humus and clay-organic complexes is the separation of the amount of indicator dye, in this case methylene blue, (1) physically adsorbed on the surface from (2) that involved in cation exchange. Kipling (1965, p. 264) notes in some systems where dyestuffs are adsorbed by two such mechanisms: (1) reversible physical adsorption is a function of dye concentration; whereas (2) adsorption involving equivalent quantity of cations is independent of the dye concentration. Thus measurements of various samples taken with a constant dye concentration should be indicative of the CEC, although this procedure would assume a uniform physical adsorptive capacity in the natural material.

Robertson and Ward (1951) developed and reported a rapid method for measuring the CEC of clay using methylene blue (see Appendix I for description of methylene blue).

Their method requires about five minutes to perform and is a relatively simple laboratory operation. Fairbairn and Robertson (1956, p. 129) applied the method to soil testing and conducted comparison between the methylene blue test with other methods of measuring CEC. They reported that when twice the amount of dye required to satisfy the CEC is present, the clays adsorb a further amount of dye. They expressed this amount as a percentage of the CEC, for example kaolinite 5% and 12%, calcium smectites (montmorillonite) 10%. They also report large variation in CEC obtained from the same clays by the different methods of measurement so that it is difficult to determine the accuracy of the methylene blue test. In their comparison with the ammonium method alone, methylene blue appeared to give comparable results for smectites, illites, and lithium-treated vermiculites. The methylene blue method did not measure the full CEC of peat, zeolites, glauconite, the impurities of diatomite or organic ion exchangers. The method did give twice the ammonium value for Vallecas sepiolite, but in this case they concluded that the calculated value agrees with the methylene blue test.

Adsorption of dyes by clay minerals has received considerable attention over the past 30 years (Faust, 1940; Bossazza, 1944; Bradley, 1945; MacEwan, 1948; Mackenzie, 1948; Emodi, 1949; Grim, 1953; Hauser, 1955; Ramachandran et al., 1961a, b).

Ramachandran et al. (1962, p. 1965) reviewed this literature and reported: "Much of the work on clay-organic complexes pertains to reactions between montmorillonite and halloysite and various organic compounds. Hendricks (1941) and Grim et al. (1947) found that small organic molecules replaced the exchangeable cations on montmorillonite quantitatively, but with larger molecules the exchange is incomplete due to the 'cover up effect'.

In general, the cation exchange capacity (CEC) values of clay minerals obtained by methylene blue adsorption are far less than those obtained by other standard methods (Worral, 1958; White and Cowan, 1960; Robertson and Ward, 1951). Much discrepancy is reported between surface areas calculated by methylene blue adsorption and B.E.T. methods (Kipling and Wilson, 1960).

In spite of a large amount of work there is still confusion about the exact mechanism involved in the adsorption of dyes by clay minerals."

They discuss the studies on adsorption of three basic organic dyes: malachite green (MG), methylene blue (MB) and methyl violet B (MV) on three groups of clay minerals: kaolinite, illite and smectite, and offer explanations of the cation exchange properties and orientation of molecules after adsorption. Their findings are summarized in Table I.

In the absence of significant concentrations of organics, the CEC by the MB method and ammonium acetate method agree quite well for kaolinite and illite. The MB method for smectites was 20—40% lower than the ammonium acetate values. Their data indicate that the broken bonds of smectite (about 20% of its CEC) are exchanged proportionately for MB changes in adsorption on that clay, although broken bonds are responsible for a relatively small proportion of its total exchange capacity. However, MB exchanged on the interlayer position in smectites apparently is large enough to mask more than one equivalent exchange site so that less total MB is exchanged than indicated by specific absorp-

TABLE I

Cation exchange capacities of clay minerals by various dyes (after Ramachandran et al., 1962)

Clay minerals	Ammonium acetate	Malachite green		Methylene blue		Methyl violet	
	CEC*[1]	CEC	percent*[2]	CEC	percent*[2]	CEC	percent*[2]
Kaolinite – I	7.12	10.23	144	7.03	99	6.77	95
Kaolinite – II	6.00	6.65	111	5.94	99	6.29	105
Illite	27.00	15.01	56	26.00	96	19.48	72
Montmorillonite – I	80.61	26.77	33	64.07	79	62.15	77
Montmorillonite – II	77.21	22.60	29	58.34	76	48.22	63
Montmorillonite – III	93.00	30.21	32	59.70	64	58.40	63

*[1] Cation exchange capacities, CEC, are expressed as mequiv./100 g.
*[2] CEC as percent of value determined by ammonium acetate.

tion observation. Furthermore, according to R. L. Malcolm (personal communication, 1971) the ammonium acetate method is a poor standard to evaluate the MB method for: (1) illites, as degraded illites fix NH_4^+ so give low exchange values; and (2) vermiculites, where NH_4^+ in the interlayer position traps other exchangeable cations, so complete replacement may require days or weeks, again giving low CEC values.

Recent investigations on the adsorption of MB on kaolinite by Faruqi et al. (1967, p. 28) tend to confirm the earlier findings that MB is more completely adsorbed on kaolinite than on smectite. They indicate that the intracrystalline surfaces of smectite may not be available to the MB molecule.

Adsorption of methylene blue by silica and quartz

Allingham et al. (1958, p. 108) investigated the mechanism of adsorption of aromatic solutes, especially dyes, by silica. They reported that the rate of adsorption of basic dyes on silica is very high, and that micellar adsorption of methylene blue does occur. They concluded that basic dyes are adsorbed by ion-exchange in the form of a monolayer of cationic micelles, the amount absorbed being considerably in excess of that required to cover the surface with a normal monolayer.

Application of methylene blue to water testing

In 1964, Kim et al. (1965) developed a technique for measuring the CEC of the floc produced in the coagulation process of water treatment. Their procedure is as follows:

To 100 ml of clay suspension, appropriate volumes of 1 mg/ml MB are added and mixed. The floc is filtered on a 0.45 μ membrane. The first 50 ml are discarded and the next 25 ml are collected for optical density measurements using a 2-cm cell spectrophotometer at appropriate wave length, 400–600 mμ dependent upon standardization curve employed. The difference between initial and filtrate dye concentration was taken as representing the microequivalents of MB adsorbed per litre. Values for 10–80 μe/ℓ were measured. This method appears to be applicable to the measurement of CEC in sea water.

EFFECT OF SEA WATER ON CLAY MINERALS

Carroll and Starkey (1958, pp. 84–99) studied the reactivities in sea water of clay minerals, using 1:50 clay-sea water suspensions, and they observed the same kinds of exchange mechanisms that have been found experimentally for electrolytes. The replaceabilities of H^+ ions on clay minerals examined follows the order $Ca^{2+} > Mg^{2+} > Na^+ > K^+$, but Mg^{2+} commonly makes up a larger proportion of the cations in the exchange positions than Ca^{2+} because there is more magnesium than calcium in sea water. They also observed solution of silica from the clay minerals, as well as a significant change in the total cation exchange capacity of the clay minerals with long-term exposure to sea water. They determined the CEC of the clay minerals by leaching them with 1 N NH_4Cl solution and assayed the leachate for the exchanged cations. Their tests were performed using 1-g samples of clay minerals separated from 50 ml of sea water by centrifugation.

METHYLENE BLUE METHOD FOR CEC DETERMINATION IN SEA WATER

A series of tests were performed: (1) the optimum light wave for conducting the CEC measurement; (2) the adsorbance of MB on the filter membrane; (3) the adsorbance of MB with: (a) natural sea water containing organic material; (b) artificial sea water without organics; and (c) distilled water in order to establish the behaviour of MB. A standard curve or calibration curve of the optic system for different MB concentrations also was prepared. Procedural steps for the MB method are given in Appendix II.

The test materials were: sea water filtered through a 0.45 μ pore diameter filter, glassware rinsed with MB concentration of approximately the same as the test concentrations used in each glass article, and artificial sea water[1] with a salinity of 34‰. The MB was prepared with Baker[2] reagent lot no. 1-2276 by drying 24 h at 105°C, dissolved in distilled water to produce a primary solution of 10μe/mℓ preserved with a few drops of chloroform. The primary solution was diluted to 0.1 μe/ml in filtered sea water for a working reagent to be added to sea water to perform the CEC measurement and for preparation of the calibration curve. Filtered (0.45 μ) sea water was used to prepare the calibration curve. The sea water was collected 1.5 nautical miles west of Point Montara on 6 February 1968. The laboratory tests were conducted at room temperature, 20°–23°C and the samples were refrigerated except during testing.

Tests showed the optical density of the filtrate did not change significantly between 10°C and 30°C. However, the temperature of the dye-sea water mixture during adsorption and filtration was found to be critical. Tests performed at 15°C resulted in CEC of

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[1] Dayno Synthetic Sea Salt, product of Dayno Sales Co., Lynn, Massachusetts.

[2] "Baker Analyzed" Reagent, product of J. T. Baker Co., Phillipsburg, New Jersey.

TABLE II

Light absorption by MB in sea water, 20°C, 25 mm Path, 0.4 µe/ℓ

Wave length mµ	T/T_0 × 100
640	93.5
625	93.5
600	93.0
575	96.5
550	97.5
525	98.5
500	98.5
450	97.5
400	97.5

TABLE III

MB adsorption on Millipore* filter membrane from distilled water (20°C, 0.002 µe/mℓ MB)

Increment of dye (mℓ)	Average filtered volume (mℓ)	T/T_0 × 100
10	–	–
20	20	92.0
20	40	85.5
20	60	82.3
20	80	81.2
20	100	80.8
20	120	81.2
20	140	81.7
20	160	80.2
20	180	80.0
–	unfiltered	77.2

*The Millipore Filter; a product of Millipore Filter Corp., Bedford, Mass.

0.55 µe/ℓ, 20°C, 0.6 µe/ℓ; at 25°C, 0.65 µe/ℓ and at 35°C, 0.75 µe/ℓ. No correction for evaporation during vacuum filtration was made.

The wave length selected for maximum light adsorbence was 600 mµ. Other values considered are shown in Table II. The results of the test for saturation of the filter membrane using the concentration of MB for testing is presented in Table III. Fig.1 shows that 90% equilibrium adsorption has occurred with a filtered volume of 60 ml for a 47 mm diameter filtering surface. The equilibrium value observed, $T/T_0 \sim 0.80$, contained approximately 15% less dye in the filtrate than was present in the unfiltered sea water. It was assumed that MB adsorption on colloidal silica and other artifacts in the distilled water used to make the artificial sea water resulted in this difference.

Unquestionably if the CEC of suspended material varied appreciably from sample to

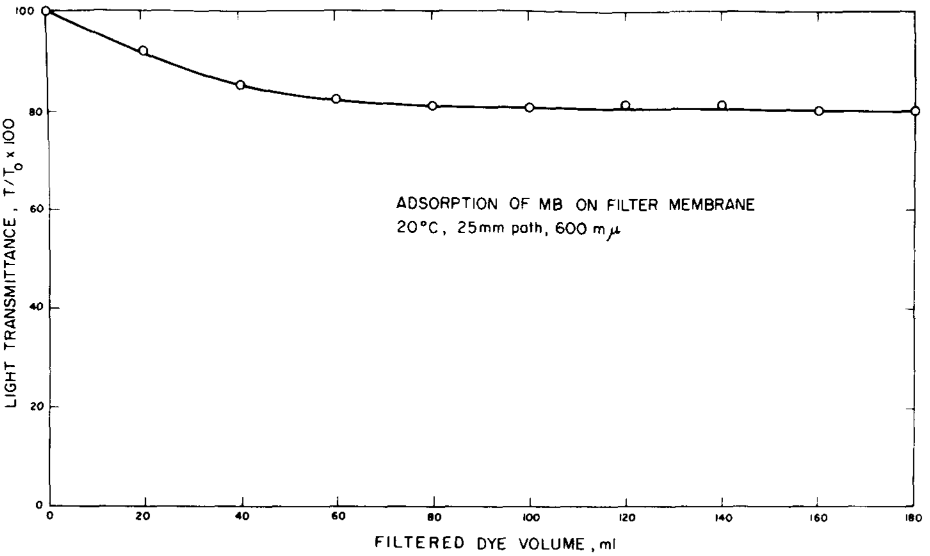

Fig.1. Exchange equilibrium between MB and filter membrane.

sample, the rate of adsorption of MB by the filter might change. Thus the equilibrium adsorption would occur at different through-put volume. R. L. Malcolm (personal communication, 1971) suggests that this problem of filter sorption may be avoided by centrifuging the sample-dye mixture instead of filtering to separate the particulate matter. Also presaturation of the filter should reduce this error.

A sample of sea water containing 5.2 μe/ℓ CEC was tested and refiltered to evaluate the amount of CEC on colloids passing through the filter. A single filtration of the dye-filtrate mixture resulted in the removal of 0.4 μe/ℓ CEC. Repeated filtration of a sea-water sample containing 0.65 μe/ℓ CEC resulted in a 6% increase in the observed CEC on each of four filtrations following the initial filtration. A total of 25% increase in removable CEC was observed at the 0.65 μe/ℓ level for four additional filtrations or 0.05 μe/ℓ for a single refiltering.

Precision

The precision of the MB method was evaluated by testing 10 replicate samples at the 0.7 μe/ℓ level and one standard deviation, σ, was found to be ± 0.05 μe/ℓ.

The calibration curve shown in Fig.2 and Table IV was prepared at 20°C. The standard solution was prepared in natural sea water and in artificial sea water. It is recommended that local filtered sea water be used for preparing the standard curve.

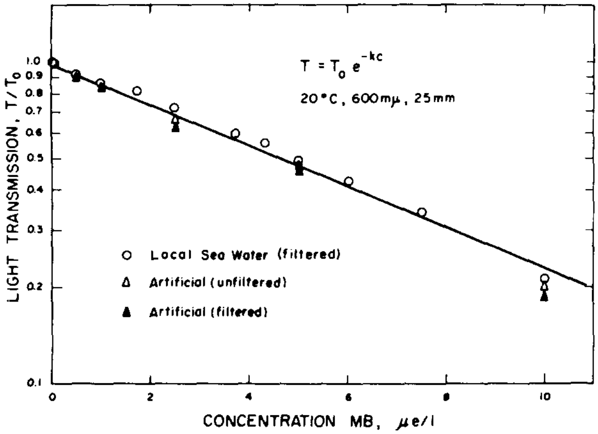

Fig. 2. Standard curve for MB in filtered sea water.

TABLE IV

Standard curve, MB in filtered sea water (20°C, 600 mμ and 25 mm Path)

Concentration of MB, μe/mℓ	$T/T_0 \times 100$		
	natural sea water	artificial sea water	
		A*	B*
0	100.0	100.0	100.0
0.000,1	99.8	–	–
0.000,5	91.7	91.7	91
0.001,0	87.5	85.3	85
0.001,7	81.9	–	–
0.002,5	72.0	67.5	63.8
0.003,7	60.0	–	–
0.004,3	55.8	–	–
0.005,0	49.0	48.5	47.0
0.006,0	42.5	–	–
0.007,5	34.0	–	–
0.010,0	21.0	20.0	18.5

*Artificial sea water prepared from Dayno Synthetic Sea Salts
Sample B preserved with Zephrin chloride and filtered.

Accuracy

As noted above both organic and clay components of suspended matter have CEC. Particulates are about 60% organic in the onshore Pacific and about 30% organic in offshore areas (Parsons, 1963, p. 220). The relative exchangeability of MB with these organics is not known. However, by analogy with soil humus the CEC for organics is about 3 times that of montmorillonite or 30 times that of kaolinite (compare values in Table I with values reported by Russell, 1961, p. 282). Malcolm and Kennedy (1970) have shown that macro-organic particulates in streams have slow exchange rates, requiring hours to days to reach equilibrium. As the particulates in sea water encountered in this study are microscopic, this slow reaction phenomenon should have no influence on the measured CEC. In the absence of both detailed studies of the CEC of organic particles and exact knowledge of composition of organic particles in sea water, only the accuracy of the method with respect to the clay content or on an organic free basis can be discussed with any authority.

The CEC of clay-type particulate matter as noted in Table I is a function of clay type. Thus the value of CEC by MB/CEC absolute for clays free of organics will be less than one if the suspended load contains significant smectites. In addition, the described MB method has an inherent inaccuracy of about 5% (Appendix II). Therefore, for 100% clay mineral organic free the following ratios hold:

Clay mineral	*CEC MB/CEC absolute*
kaolinite	$\geqslant 0.95$
illite–mica	$\geqslant 0.90$
smectites	$\geqslant 0.60$

In areas of low smectite introduction into sea water such as the tropics (see Gibbs, 1967, p. 1224), the CEC by the MB method should be approximately equal to the absolute CEC. However, in mid-latitudes, the smectite contribution to the sea by rivers is high. This picture is further complicated by the fact that illites and chlorites degraded in the weathering process act like smectites. The combination of smectites and degraded clays would lower the CEC measured by the MB method particularly in the nearshore environment, before the degraded clays had the opportunity to fix potassium from the sea water.

There is insufficient data on the comparison of the clay mineralogy of bottom sediments with the suspended load of the water column immediately above, so nothing more than regional generalities can be made concerning the CEC. We suggest, if possible, that the clay mineralogy be determined for each sample to give a better idea of the accuracy of the CEC by MB method. For the small volumes of samples we used, it was impossible to obtain recognizable X-ray diffractograms.

Application of methylene blue method

To test the validity of the technique in the marine environment, sea water samples were collected from the surf zone along the central California Coast from the nearshore turbid region and from clear water further offshore as shown in Fig.3.

The surf samples were collected in the swash zone at the beach in a plastic bucket. The offshore samples were collected by means of a Kemmerer sampler from a depth one meter beneath the ocean surface. The sea water used to develop the standard curve was pumped into a 20 litre container from a depth of one to two meters. The samples were taken to the

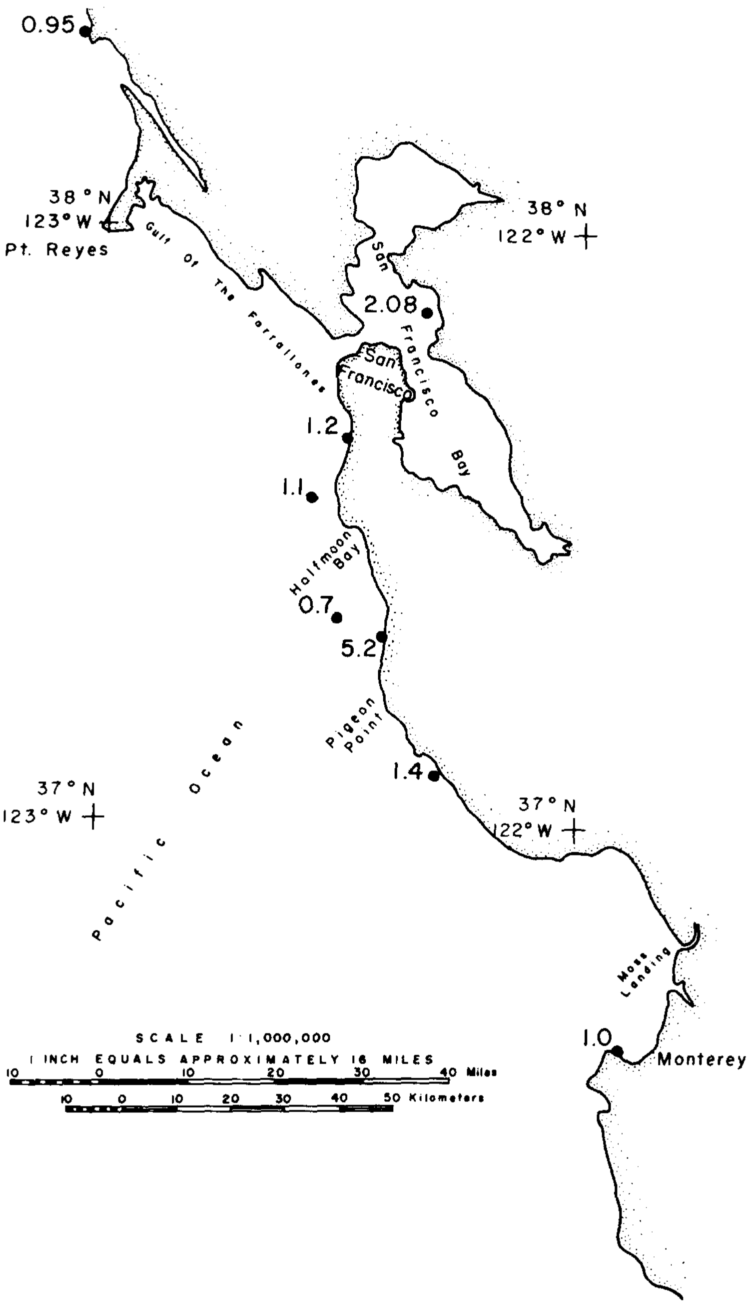

Fig.3. CEC values off the central California coast. Values of CEC in $\mu e/\ell$.

TABLE V

Cation exchange capacity of suspended material in sea water, central California, 600 mμ, 25 mm Path.

Sample description	Light transmission $T/T_0 \times 100$		Exchange capcity μe/ℓ
	unfiltered	filtered	
Sea water, 3.5 miles west Tunitas Creek – 9.5 miles south Half-Moon Bay	73.5[*1]	82.0	0.7
1.5 miles west Point Montera	62.7[*2]	75.0	1.1
Surf, Pacifica	74[*1]	88	1.2
Surf, San Gregorio Creek	51.5[*3]	89	5.2
Surf, Santa Cruz County Line	77[*1]	91	1.4
Hopkins Marine Station – Pacific Grove	73[*1]	85	1.0
Bodega Marine Laboratory[*4]	84.2[*1]	92.1	0.95
Berkeley Pier San Francisco Bay[*4]	76.3[*2]	93.1	2.08

[*1] Initial concentration of MB was 2 μe/ℓ.
[*2] Initial concentration of MB was 3 μe/ℓ.
[*3] Initial concentration of MB was 6 μe/ℓ.
[*4] From Latty (1970).

laboratory in polyethylene containers and refrigerated several days prior to testing. The list of samples and the test results are presented in Table V.

Surf zone samples from areas of no local stream discharge had CEC's of 1 μe/ℓ (Hopkins Marine Station), 1.2 μe/ℓ (Pacifica), and 1.4 μe/ℓ (Santa Cruz–San Mateo County Line). Offshore samples had CEC's of 0.7 μe/ℓ (3.5 miles offshore). The sample collected from the surf near the mouth of San Gregorio Creek had a significantly higher CEC, 5.2 μe/ℓ, presumably due to increased clay content in winter stream discharge.

The MB technique is satisfactory for surface and nearshore waters that contain at least 0.8 mg/ℓ suspended material. However, the amount of suspended particulate matter (0.04–0.15 mg/ℓ: Jacobs and Ewing, 1969; 0.01 mg/ℓ; Eittreim and others, 1969, p. 617) in deeper pelagic water is apparently less than the amount of material with sufficient exchange capacity detectable by the MB technique.

The CEC values listed in Table V are on the order of μEq/ℓ (range 0.7 to 5.2 μEq/ℓ). On the other hand the alkalinity of sea water is about 2 mEq/ℓ (Harvey, 1963, p. 160) or about 10^3 times that of the CEC of the suspended matter. According to Sillén (1961) the aluminosilicates (clays) in suspended matter can break down such that 1 mg of clay can yield 0.01 mg hydrogen ion. Accordingly the minimum amount of suspended matter 0.8 mg/ℓ detectable in the MB method would yield 8 μEq/ℓ or 80 times that of the CEC of 0.1 μEq/ℓ. If this relationship of Sillén type buffer to CEC holds over the range of observed CEC values of Table V, then, assuming the suspended particles are all clay and the alkalinity is constant, the maximum proportions of alkalinity to Sillén buffer to CEC is 2000:416:5.2. This substantiates the view (Pytkowicz, 1967, p. 70) that at least for the water column the pH of sea water is controlled by carbonate buffer reactions and not by silicate (clay) reactions or simple cation exchange on non-reacted clays. However, as most of the insults to the ocean occur at water-sediment boundaries at river mouths and orifices of sub-sea volcanoes, the Sillén silicate buffer model cannot be discounted where sediment as clay is essentially in infinite supply, and where sea water–interstitial water interactions are permitted by bottom current and tidal reworking of sediment or by bioturbation.

CONCLUSIONS

(1) The methylene blue, MB, method developed for the determination of cation exchange capacity, CEC, of suspended material in sea water is sensitive for values between 0.1 μe/ℓ and 10.0 μe/ℓ.

(2) Several nearshore sea water along the central California coastline contained 1 to <6 μe/ℓ CEC.

(3) At best this method gives an apparent CEC determined not only by MB exchanged on organic, clay-organic, and clay particles but also of MB physically absorbed on the particles. We believe the ease of sampling and rapidity of measurement make this method give a useful approximation of the CEC of particulates in sea water, outweighing the uncertainties caused by the lack of detailed information on the absorptive and exchange behaviour of organic particles in sea water.

APPLICATIONS

(1) The technique developed for the CEC of sea water should find some application in pollution control in instances where suspended material was being discharged to the sea. In this case the CEC should be significantly higher than background due to the high organic content of waste water discharged from an outfall.

(2) This rapid MB technique can be used on organic free samples to evaluate various diagenetic changes of clay particles in sea water and test various Sillén (1961) type silicate sea water buffer models.

APPENDIX I

The nature of methylene blue

Taylor (1935) and Faruqi et al. (1967, p. 19) described methylene blue (MB) molecule as the para-quinonoid structure shown (Fig.4) and determined its arrangement in the crystallized compound. The molecule, although lath-like, is not certainly flat. It can be accompanied by water of crystallization.

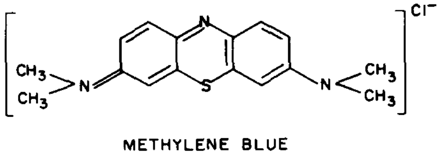

Fig.4. Methylene blue radical (after Faruqi, 1967 and Taylor, 1935).

Warwicker (1955) obtained results agreeing generally with those of Taylor (1935) but found that several hydrates exist, each presumably stable within a certain humidity range.

Methylene blue (MB^+) is a cationic and organic dye that does not hydrolyze in the manner of Al^{3+} or Fe^{3+}. Jenny (1935) suggested that MB^+ is more strongly cationic than any inorganic cation that it will displace Ca^{2+}, Mg^{2+}, $NH_4{}^+$ etc. Commercial MB^+ is a chloride salt with three benzene rings and with a dehydrated molecular weight of 319.9.

APPENDIX II

MB procedure

(1) To 100 ml of sea water add 2 ml of dye solution containing 0.1 μe/mℓ MB, mix.

(2) Filter 80 ml through a 0.45-μ pore diameter filter. The first 60 ml are wasted and the following 20 ml are retained for estimation of the CEC of the suspended material in the sea water that is retained on the filter. The unfiltered remaining 20 ml is used for initial light adsorption observation.

The value of the initial light transmittance for the unfiltered portion is not used in the calculation of the CEC of the sea water as the initial dye concentration is known, but the decrease of light transmittance for the concentration used from the expected value is a measure of the turbidity of the sample, and an anomalous value may assist in interpreting of any unusual results.

(3) Determine the light transmission at a wave length of 600 mμ using a 25-mm diameter light path. The milliequivalents of MB dye remaining are read from the standard curve in Fig.2.

(4) The amount of dye added minus the amount of remaining dye following filtration is the CEC of the suspended material in the sea water. No correction for filter equilibrium is made. The value is reported as μe/ℓ CEC.

(5) Filtered samples having percent transmittance greater than 90% should be repeated at higher dye concentrations.

APPENDIX III

Filter accuracy

Positive error

For 0.2 μe MB added to sea water $T/T_0 \times 100$ is 80–90% after filtration so the dye removal will be about 0.05 μe. The filter absorption equilibrium is 10% less (Fig.1) at a filtered volume of 60 ml. Thus the dye concentration passing the filter is 10% of 0.05 μe or 0.005 μe too high.

If the true exchange capacity is 0.15 μe, then the observed value would be 0.155 μe or:

$$100 \times \frac{0.155-0.150}{0.150} = 3\text{–}1/2\%$$

This error is positive due to dye absorption by the filter.

Negative error

The material $< 0.5\ \mu$ which passes the filter has some exchange capacity which, of course, is not accounted for by the method. At the 0.62 μe/ℓ level this loss is $\frac{0.2}{0.62} \times 100 = 32\%$; at the 5.2 μe/ℓ level this loss is $\frac{0.4}{5.2} \times 100 = 7.7\%$.

Inherent inaccuracy

The sum of the error due to the properties of the filter, for realistic conditions, would be + 3%–8% = –5%.

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