Notes

Development of an Automatic pH Adjustment Instrument for the Preparation of Analytical Samples Prior to Solid Phase Extraction

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An automatic pH adjustment instrument was developed for the preparation of analytical samples prior to solid phase extraction, which is widely used as a pretreatment technique for the separation of sample matrixes and preconcentration of elements for analysis. Real-time monitoring of the sample pH condition was performed by observing the light signal intensity of the pH-sensitive wavelength of the pH indicating reagent. A light of pH-insensitive wavelength was selected as the reference light to cancel the signal intensity variation of the pH-sensitive light due to the difference of pH indicating reagent concentration, possible difference in transparency of sample vessels, and minute fluctuation of the light source. The pH condition was elevated by automatic addition of ammonia solution using a nebulizer in the flow line of which an electromagnetic valve was equipped. Open and close operation of the electromagnetic valve was controlled based on the difference between the real-time pH condition and the target pH condition. The effectiveness of the instrument was confirmed by using various pH indicating reagents and by analyzing trace elements in a seawater certified reference material.

Keywords Automatic pH adjustment instrument, solid phase extraction, pH indicating reagent, spectrometer, nebulization

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Introduction

Solid phase extraction (SPE) is an effective approach for the separation of sample matrix and the preconcentration of the analytes in chemical analysis. SPE techniques using chelating resins have been widely investigated as sample pretreatment methods for trace elements prior to their measurement.[1-39] Due to the mechanism of SPE with chelating resin, *i.e.* adsorption of trace elements to the resin at weak acidic to neutral pH conditions and desorption from the resin in strong acidic conditions, the optimum pH conditions reported for adsorption were usually 5,[1-8] 5.5,[9-14] 5.7,[15] 6,[16-27] 6.13,[28] 6.5,[29,30] and 7.[31-33] There have also been several works reporting multiple pH conditions, *e.g.* 4.0 – 7.0,[34] 5.0 and 6.0,[35] 5.5, 6.5, and 8.5,[36] 6, 7, and 8,[37] 6.0 – 7.0,[38] and 6.0 – 7.5.[39] Such optimum conditions depend on the chemical property of the target element and the sample matrix as well as the functional group and the chemical structure of the chelating resin. Nevertheless, the optimum pH conditions were most often chosen in the pH range from 5.0 to 7.0 as indicated by the aforementioned reports.

The precise adjustment of a solution to neutral pH condition requires the precise controlling of H^+ concentration at the 10^{-6} to 10^{-7} mol L^{-1} level. Therefore, great attention should be paid for manual adjustment of pH for SPE with chelating resins. A commercially available preconcentration system, *i.e.* seaFAST (Elemental Scientific), provids an approach for pH adjustment by diluting the sample with an ammonium acetate buffer.[40-45] Due to the limited naturalization capability of ammonium acetate buffer, the samples after pH adjustment usually had high concentrations of ammonium ions and acetate ions. They may compete with the cations of trace elements and the functional groups of the chelating resin, respectively, during the SPE operations. Apparent lower recoveries for some elements reported might be attributed to the competition with such cations and anions.[41,44,45]

As an alternative approach for precise pH adjustment in SPE operations with chelating resin, the authors developed an automatic pH adjustment instrument and applied it to the measurement of rare earth elements (REEs) in seawater samples.[46] In the automatic pH adjustment instrument, the pH of a sample solution with pH indicating reagent (methyl-red) was monitored by measuring the transmitted light, based on a pre-established correlation between the pH and the transmitted light-intensity. Such non-contact monitoring of the pH condition of the sample avoided possible contamination from a pH electrode. The addition of ammonia solution for elevating the pH from acidic to neutral condition was precisely controlled by a nebulizer (usually used in inductively coupled plasma techniques) and an electro-magnetic valve, permitting a precise addition of ammonia solution at less than 0.1 μL. Real-time monitoring of the pH condition based on transmitted light and precise controlling of ammonia solution permitted the precise pH adjustment for SPE operations with chelating resins. The instrument was applied to the analysis of REEs in seawater

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samples. However, it was found later that the transmitted light based pH monitoring required high reproducibility of the container light-transparency as well as a precise concentration of pH indicating reagent in the sample.

In the present work, the automatic pH adjustment instrument was improved to achieve a precise pH adjustment independent of the concentration of pH indicating reagent in the sample solution. An application of the present automatic pH adjustment instrument had been preliminary reported and referred to as "electrodeless pH controller".[47] Technical details about the automatic pH adjustment instrument are presented in the present work along with the application to the determination of multiple trace elements in a seawater certified reference material (CRM).

Experimental

Instruments

An ICP-MS instrument (Agilent 8800s type) was applied for the analysis of trace elements. The operating conditions of the ICP-MS were optimized daily to achieve relatively high signal intensities for the elements of interest. Typical operating conditions of the ICP-MS can be found in Supporting Information (Table S1). Hydrogen gas was used as the reaction gas for effective removal of polyatomic interferences, e.g. $^{40}Ar^{16}O^+$ with the measurement of $^{56}Fe^+$, and $^{94}Mo^{16}O^+$ with the measurement of $^{110}Cd^+$.

Reagents and chemicals

Metrological traceable single element standard solutions were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). The traceability of the standard solutions were guaranteed by the Japan Calibration Service System (JCSS). Ultrapur® HNO_3, ammonia solution, acetic acid and reagent grade ethanol were also purchased from Kanto Chemical Co., Inc., and used for preparing the solutions in the present experiment. Reagent grade bromophenol-blue, bromocresol-green, methyl-red, and phenol-red were also purchased from Kanto Chemical Co. Inc. to prepare solutions of pH indicating reagents.

A seawater CRM was purchased from the National Research Council of Canada. Chelating resin columns, NOBIAS Chelate-PA1 (M-size), were purchased from Hitachi High-Tech Fielding Corp. (Tokyo, Japan).

Construction of the automatic adjustment instrument

The structure of the automatic pH adjustment instrument is illustrated in Fig. 1. As can be seen from Fig. 1, the light from light source (1) transmitted through the sample (2), which was mixed with a magnetic rotor (3) driven by a magnetic stirrer (4) at 100 revolutions per minute. The transmitted light was measured by a spectrometer (5), which sent a signal to the I/O board (6) and then to the controlling computer (7). Based on the correlation between the signal intensity ratio of a pH-sensitive light to a pH-insensitive light and the pH condition, the controlling computer sent open/close commands to the I/O board (6) and then to the electro-magnetic valve (8). The open/close operation of the electro-magnetic valve (8) controlled the supply of ammonia solution (9) through the nebulizer (10) to the sample solution (2), where the addition of ammonia solution (2) through the nebulizer (10) was driven by the air (11) with a flow rate of approximately 1.0 L min⁻¹ and resulting in an uptake rate of ammonia solution at 0.5 mL min⁻¹, where an in-line filter was equipped to prevent contamination from the atmosphere.
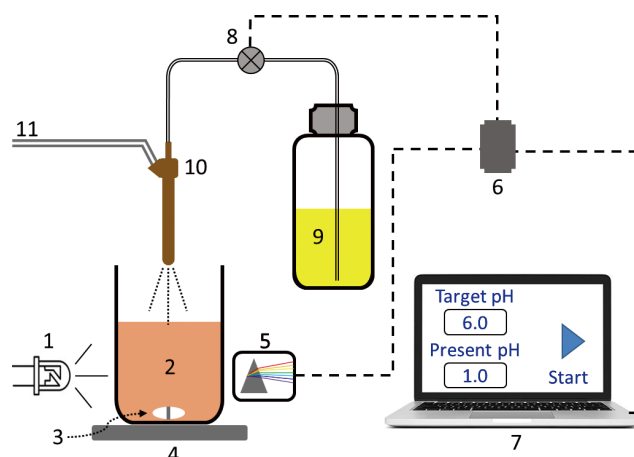

Fig. 1   Structure of the automatic pH adjustment instrument.   1, Light source; 2, sample; 3, rotor; 4, magnetic stirrer; 5, spectrometer; 6, IO board; 7, computer; 8, electro-magnetic valve; 9, ammonia solution; 10, nebulizer; 11, air.

Flow chart for the automatic controlling program

The typical operation of the automatic controlling program for the instrument is illustrated with a flow chart in Fig. 2. As can be seen from Fig. 2, the valve was closed and the target pH value (A_t) was read after starting the adjustment. The signal intensities of pH-sensitive light (^aI_i) and pH-insensitive light (^rI_i) were read from the spectrometer. Then, the current pH value (A_i) was calculated from the signal intensity ratio of ($^aI_i/^rI_i$). The difference between the values of A_i and A_t was calculated as ΔA, which was compared with 0.0 so as to evaluate whether the target pH was achieved. It is notable that water samples for trace elements analysis are usually stored at relatively strong acidic conditions with pH lower than 1.0. The purpose for adjustment of pH condition for SPE operation is usually to elevate the pH value, i.e. "$A_i < A_t$" in the beginning of the pH adjustment.

When the target pH was not achieved, i.e. "$\Delta A = 0.0$" was not satisfied, the value of ΔA was further compared with 0.6, 0.4, 0.3, 0.2, and 0.1 in turn. When the value of ΔA was over 0.6, the valve was kept open, permitting introduction of ammonia solution into the sample to elevate the pH value until the next round of calculations of A_i and evaluation of whether "$\Delta A = 0.0$". When the condition of "$0.6 \geq \Delta A > 0.4$", "$0.4 \geq \Delta A > 0.3$", "$0.3 \geq \Delta A > 0.2$", "$0.2 \geq \Delta A > 0.1$", and "$0.1 \geq \Delta A > 0.0$" was respectively satisfied, the valve open/close times (unit, ms) were respectively set to 3000/2000, 2000/2000, 1000/1500, 500/2000, and 150/2500 until the next round of calculations of A_i and evaluation of whether "$\Delta A = 0.0$". The open/close time sets were optimized to permit the sample to become completely mixed after each round of ammonia solution addition, as well as to avoid over addition of ammonia solution.

When the target pH was achieved, i.e. "$\Delta A = 0.0$" was satisfied, the valve was closed and the program of pH adjustment ended.

Procedure for SPE preconcentration with chelating resin

The typical procedure for SPE preconcentration with chelating resin used in the present work was as follows. The chelating resin columns (NOBIAS CHELATE-PA1) were washed with 5 mL of 3 mol L⁻¹ nitric acid and 5 mL of pure water, followed by conditioning with 5 mL of 0.1 mol L⁻¹ ammonia acetate. Then, 50 mL of the sample (with 100 μL of 0.4 mg mL⁻¹
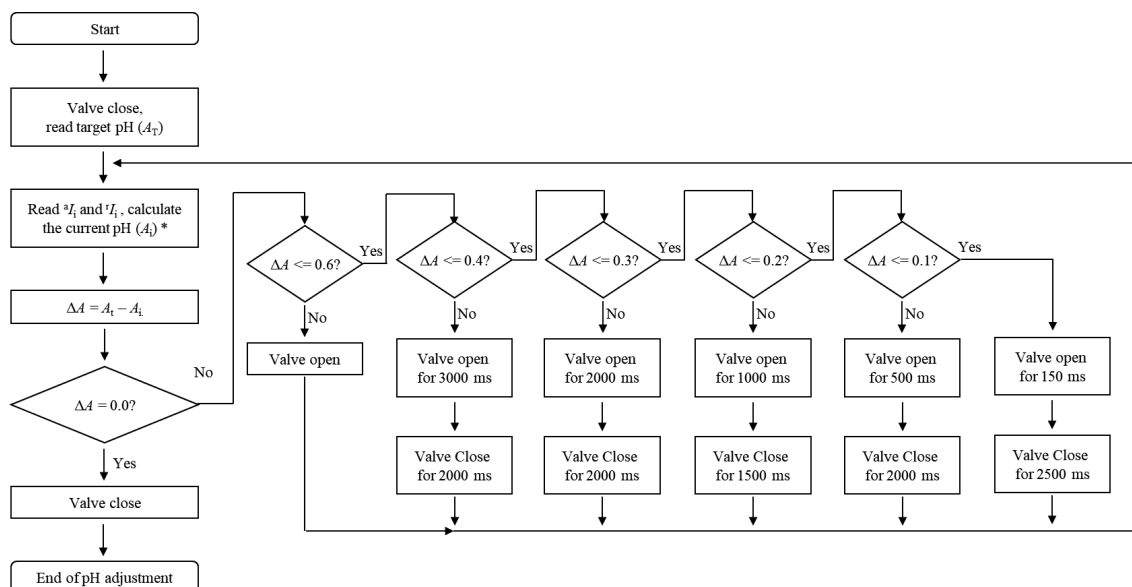
Fig. 2   Flow-chart for automatic pH adjustment. *, ^aI_i and ^rI_i, indicate signal intensities of the pH-sensitive light and the pH-insensitive light, respectively.

methyl-red in ethanol as pH indicating reagent) adjusted to pH 6.0 was loaded to the chelating resin column at a flow rate of approximately 10 mL min^{-1}. After sample loading, 10 mL of 0.1 mol L^{-1} ammonia acetate and 5 mL of pure water were passed through the chelating resin column for washing. Finally, trace elements adsorbed on the resin was eluted with 5 mL of 2 mol L^{-1} nitric acid and then subjected to the measurement by ICP-MS.

The samples for blank test and recovery test were also subjected to the same procedure for SPE preconcentration.

Quantitation of trace elements was carried out based on a gravimetric-based standard addition method following the procedure described in a previously reported work.[48] An yttrium standard solution was spiked to each sample in the present work to achieve a concentration of 1 ng mL^{-1} yttrium in the sample solution prior to pH adjustment. The signal of $^{89}Y^+$ was measured as the internal standard.

Results and Discussion

Effectiveness of a reference light for ensuring the stability of pH adjustment

In the present work, a light of pH-insensitive wavelength was used as the reference light to cancel the variation of brightness of the sample solution, probably due to the minute variations in the concentration of pH indicating reagent and the transparency of sample vessels.

The effectiveness of a reference light for ensuring the stability of pH adjustment was confirmed by using methyl-red as the pH indicating reagent and by setting the target pH value to 6.0. Based on the absorption properties of methyl-red as a pH indicating reagent shown in Fig. 3, the pH-sensitive wavelength and the pH-insensitive wavelength were chosen at 530 and 620 nm, respectively.

The calibrating curve for calculating the pH value from the signal intensities at the pH-sensitive wavelength and the pH-insensitive wavelength were obtained by addition of 100 μL methyl-red (0.4 mg mL^{-1} in ethanol) to each 50 mL of coastal
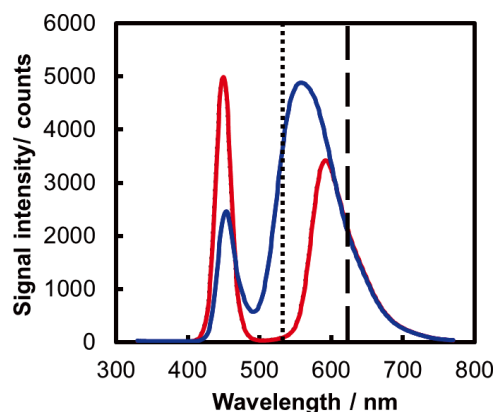

Fig. 3   Absorption properties of methyl-red as a pH indicating reagent. Red line profile, pH 1.0; blue line profile, pH 8.0; dotted line, pH-sensitive wavelength; dashed line, pH-insensitive wavelength. Obtained with a 50-mL coastal seawater sample with 100 μL methyl-red (0.4 mg mL^{-1} in ethanol).

seawater sample. After that, test samples (50 mL each) with 80, 100, and 120 μL of methyl-red were respectively prepared and subjected to the automatic pH adjustment. The relative difference in signal intensity of pH-sensitive wavelength at 530 nm in these samples was over 30%. After pH adjustment with the present automatic instrument, the pH values in these samples were all in the range of 5.98 to 6.00, which were sufficiently precise for SPE operations with chelating resins. When the reference light was not used, the difference in volume of methyl-red by 40 μL may result in the difference of pH value of approximately 0.3 to 0.5. These results indicate that use of a reference light was effective for ensuring the stability of pH adjustment. Therefore, a reference light was also used for pH adjustment with other pH indicating reagents.

Table 1   Typical pH indicating reagents confirmed in the present work[a]

pH indicating reagent	pH range and color	Concentration and solvent	Volume added (μL per 50 mL sample)	pH-sensitive wavelength/nm	pH-insensitive wavelength/nm	Target pH range
Bromophenol-blue	pH 3.0 – 4.6 (yellow ↔ purple)	0.4 mg mL^{-1} in ammonia solution	100	571	650	3.0 to 4.0
Bromocresol-green	pH 3.8 – 5.4 (yellow ↔ blue)	0.4 mg mL^{-1} in ammonia solution	100	573	507	4.0 to 5.0
Methyl-red	pH 4.4 – 6.2 (red ↔ yellow)	0.4 mg mL^{-1} in ethanol	100	530	620	5.0 to 6.0
Phenol-red	pH 6.4 – 8.2 (yellow ↔ red)	0.4 mg mL^{-1} in ammonia solution	100	560	610	6.0 to 8.0

a. Typical calibration curves for these pH indicating reagents are provided as Supporting Information (Figs. S1 to S4).
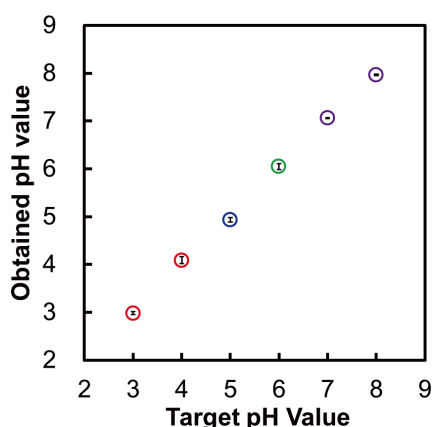

Fig. 4   Results of automatic pH adjustment. (pH indicating reagents: red circle, bromophenol-blue; blue circle, bromocresol-green; green circle, methyl-red; purple circle, phenol-red; bar in the circle, standard deviation of 3 sub-samples.)

Table 2   Blank values and ADLs obtained with ICP-MS after SPE preconcentration

Element	m/z	Blank value[a]/ng mL^{-1}	ADL[b]/ng mL^{-1}
Fe	56	0.11 ± 0.05	0.14
Co	59	0.00019 ± 0.00008	0.00025
Ni	60	0.0035 ± 0.0009	0.0026
Cu	63	0.022 ± 0.006	0.0017
Zn	66	0.087 ± 0.018	0.053
Cd	110	0.00045 ± 0.00014	0.00043
Pb	208	0.0021 ± 0.0008	0.0023

a. Mean ± standard deviation, $n = 5$.
b. Concentration corresponding to 3-fold of the standard deviation of blank value.

Typical pH indicating reagents and applicable pH range with the present instrument

Multiple pH indicating reagents were investigated in the present work to ensure the possibility of automatic and precise pH adjustment in a relatively wide pH range from 3.0 to 8.0. The characteristics of four pH indicating reagents are summarized in Table 1.

The pH indicating reagents were dissolved in ammonia solution (bromophenol-blue, bromocresol-green, and phenol-red) or ethanol (methyl-red), to obtain a concentration of 0.4 mg mL^{-1}. Typically, 100 μL of the pH indicating reagent solution was added into each 50 mL of water sample for pH monitoring. As summarized in Table 1, the characteristic lights (unit, nm) of the pH-sensitive and the pH-insensitive wavelengths for bromophenol-blue, bromocresol-green, methyl-red, and phenol-red were 580/650, 570/515, 530/620, and 560/610, respectively.

Application of the pH indicating reagents permitted the coverage of a target pH range from 3.0 to 8.0 by the present automatic pH adjustment instrument. The results of automatic pH adjustment to 3.0 to 8.0 are plotted in Fig. 4 against the target pH value assigned. As can be seen from Fig. 4, the obtained pH values were identical to the target values. The results show that the present instrument was capable for accurate and precise pH adjustment.

Analytical figures of merits

Blank values and analytical detection limits (ADLs) were

evaluated as the analytical figures of merits for trace elements obtained by ICP-MS after SPE preconcentration with chelating resin and with the present automatic pH adjustment instrument for sample preparation.

Blank values were obtained with 50 mL of 0.1 mol L^{-1} nitric acid as test samples. The test samples were subjected to the automatic pH adjustment and SPE preconcentration with chelating resin in the same way as that for the seawater samples, in which the concentration of nitric acid was also 0.1 mol L^{-1}. The final solution for analysis after SPE preconcentration was 5 mL, providing a preconcentration factor of 10-fold. The results for blank tests are summarized in Table 2, along with ADLs obtained as the concentrations corresponding to 3-fold of the standard deviation of blank values.

As can be seen from Table 2, the blank values for trace elements were in the range from 0.00019 ng mL^{-1} of Co to 0.11 ng mL^{-1} of Fe, while the ADLs were in the range from 0.00025 ng mL^{-1} of Co to 0.14 ng mL^{-1} of Fe. These values were sufficiently low for the analysis of water samples taking into consideration the regulated concentrations for these trace elements were not lower than 3 ng mL^{-1}.[49] A preliminary experiment in the present work showed that the major factor contributing to the blank values was the impurities in the solid phase of the chelating resin, while the contribution of pH adjustment was negligible.

The typical time required for pH adjustment of 50 mL of these samples was approximately 15 min. The time for automatic pH adjustment could be shorten to less than 5 min by partial neutralization of nitric acid in the sample, *i.e.* addition of some ammonia solution prior to the automatic pH adjustment.

The present instrument provided an approach for rapid and automatic pH adjustment independent to the skill of the operator.

Table 3   Analytical results and recoveries of trace elements in seawater CRM, NRC CRM CASS-5

Element	m/z	Observed value[a]/ ng mL^{-1}	Certified value[b]/ ng mL^{-1}	Spike recovery[a], %
Fe	56	1.35 ± 0.15	1.44 ± 0.11	98.8 ± 1.5
Co	59	0.093 ± 0.005	0.095[c]	97.3 ± 1.8
Ni	60	0.351 ± 0.032	0.330 ± 0.023	98.7 ± 1.3
Cu	63	0.375 ± 0.021	0.380 ± 0.028	100.2 ± 0.8
Zn	66	0.75 ± 0.05	0.719 ± 0.068	101.3 ± 1.5
Cd	110	0.0221 ± 0.0005	0.0215 ± 0.0018	100.4 ± 1.4
Pb	208	0.013 ± 0.003	0.011 ± 0.002	98.7 ± 1.2

a. Mean ± standard deviation, $n = 4$.
b. Mean ± expanded uncertainty.
c. Information value.

Manual adjustment of a sample to pH 6.0 depended on the skill of the operator, probably taking 30 min or even over 60 min to achieve a pH value in the range of 5.9 to 6.1.

Analytical results for trace elements in a seawater CRM

Trace elements in a seawater CRM, NCR CRM CASS-5, were analyzed to confirm the reliability of the present automatic pH adjustment instrument and the present analytical method. The analytical results, after subtracting the blank values given in Table 2, are summarized in Table 3 in comparison to the certified values.

As can be seen in Table 3, the observed values agreed with the certified values in the range of their expanded uncertainties. It is notable that the concentrations of these elements were at least one order of magnitude higher than the blank values and the ADLs given in Table 2, permitting accurate and precise analysis of these elements.

The spike recovery values given in Table 3 were obtained by adding a mixture of elemental standard solution so as to achieve a spiking concentration of 2 ng mL^{-1} for each element in the spiked seawater CRM sample. It can be seen from Table 3 that the recovery values were quite close to 100% with good reproducibility, *i.e.* standard deviation less than 2%.

These results indicate that the present automatic pH adjustment instrument and the present analytical method are effective for the analysis of trace elements in environmental samples including seawater.

Conclusions

An automatic pH adjustment instrument was developed for SPE preconcentration of trace elements with chelating resin. The automatic and real-time monitoring of the sample pH condition was obtained by monitoring the light signal intensity of the pH-sensitive wavelength for the pH indicating reagent. Stable pH monitoring was improved by using a reference light at the pH-insensitive wavelength for the pH indicating reagent. Automatic and precise addition of ammonia solution to the sample to elevate the pH condition to the target value was achieved by using a nebulizer, for which the flow line was controlled with an electromagnetic valve.   Open and close operation of the electromagnetic valve was controlled based on the difference between the real-time pH value and the target pH value. The results of trace elements in NRC CRM CASS-5 indicate that the present instrument was effective for automatic pH adjustment for SPE preconcentration with chelating resin.

Supporting Information

Table S1, operating conditions for ICP-MS. Figures S1 to S4, typical calibration curves for pH adjustment using different pH indicating reagents.

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