

An evaluation of quality assurance to monitor acid precipitation by using ion balance in Guizhou, China

Kang Demeng

Research Center for Eco-Environmental Sciences, Chinese
Academy of Sciences, Beijing 100085, China

Abstract—Based on methods of quality assurance to monitor acid precipitation by using ion balance proposed by US National Atmospheric Deposition Program (NADP) and National Trends Network (NTN), an ion balance calculation to acid rain data in Guizhou Province, China, and concluded that ion percentage difference is an important method in evaluating of quality assurance to monitor acid precipitation.

Keywords: acid precipitation; ion balance; quality assurance.

1. Introduction

The imbalance between the sums of cations and anions calculated on routine acid rain measurement was investigated and was considered as the result from analytical errors. However, upon the studies of Ted *et al.* (Ted, 1985) by using ion balance calculation, it was found that there are some important cations and anions were excluded in the routine measurement. The Central Analytical Laboratory (CAL) of the American National Atmospheric Deposition Program (NADP) required each analyst qualified through testing to internal quality assurance samples, and has a strict requirement on sample filtering, storing and data recording, selecting and so on. In order to achieve this object, the evaluation method of ion balance is available. All data in this paper were so chosen through internal and external quality assurance samples that to verify the feasibility of the method. through ion balance calculation to acid data of the years 1986-1988 in Guizhou with IBM-computer, the authors concluded that evaluation methods was a reliable means for the quality assurance to monitor acid precipitation.

2 Evaluation methods

There are three methods on ion balance:

2.1 Ion percentage difference of cations and anions in samples

$$I\%D = \frac{(A - C)}{(A + C)} \times 100\%, \quad (1)$$

where, $I\%D$ is the ion percentage difference of cations and anions; A is the sum of anions; C is

the sum of cations.

For NADP, $A = [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{PO}_4^{3-}] + [\text{OH}^-] + [\text{HCO}_3^-]$;

$C = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + [\text{H}^+]$.

When there is no net plus or minus charge in solution, the value of $I\%D$ for a liquid precipitation sample is zero percent, and the ratio of A/C and C/A must be 1, we give some measured data in Table 1.

Table 1 Value of $I\%D$ of some precipitation samples in Guizhou Province of China

Sample No.	Sampling month	pH	A	C	K	(A/C)-1	1-(C/A)	AVE
1	Feb.	3.97	522.4	633.9	0.09	0.1753	0.2116	0.1940
2	Feb.	3.75	380.1	526.3	0.24	0.2778	0.3846	0.3312
3	May	4.65	134.9	105.3	0.12	0.2809	0.2193	0.2501
4	May	4.79	101.4	78.3	0.13	0.2948	0.2277	0.2613
5	May	5.14	84.6	78.4	0.04	0.0793	0.0733	0.0753
6	July	6.27	80.2	68.1	0.08	0.1771	0.1504	0.1638

Note: $k = I\%D/100$; it is the average value of the data in two pre-columns

For individual precipitation sample, the $I\%D$, calculated by using measured concentration in Equation (1), may deviate from zero percent because of the following three reasons: (1) The deviation of measured concentration of cations and anions is not zero; (2) not all significant ions are measured; (3) The calculated concentration of $[\text{HCO}_3^-]$ is different from the value actually present in the sample.

2.2 The difference of measured data and calculated data of pH

For each precipitation, we can obtain the pH values by adjusting the non-conservative ions to reach the $I\%D$ near to zero, which can be done through setting the net non-conservative ion concentration ($[\text{H}^+] - [\text{OH}^-] - [\text{HCO}_3^-]$) equal to the net conservative ion concentration only when the difference of the whole ion concentration of cations and anions is very small. Since the $[\text{OH}^-]$ and $[\text{HCO}_3^-]$ are the functions of $[\text{H}^+]$, pH can be calculated by the next equation.

$$(\text{pH})_c = 6 - \log 1/2 \{ [D^-] + [D] + 4(K_1 \times K_a \times P_{\text{CO}_2} + K_w) \}. \quad (2)$$

Among the equation:

$$D = \{ [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{PO}_4^{3-}] + [\text{OH}^-] + [\text{HCO}_3^-] \\ - \{ [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] \} \} (\mu\text{eq/L}).$$

where, K_1 is the first-class ionization constant of H_2CO_3 ; K_a is the Henry coefficient of CO_2 ; K_w is the product of cations and anions in water; P_{CO_2} is the normal breach barometric pressure.

Biased pH measurement have been a rather common problem in the field of precipitation chemistry (Ted, 1985) because pH electrode can calibrate properly with commercial buffer solution and still give biases of a few tenths of a pH unit or more for rain samples, which has no evident reason according to CAL. When the calculated value of pH is near the measured value, the value of $I\%D$ is near to zero, it can be shown from Table 2. The difference of measured pH and

calculated pH is more than 0.5, which can engender the imbalance of cations and actions.

2.3 Difference of calculated conductance(*R_c*) and measured conductance(*R_m*)

The purpose of contrasting the calculated conductance and measured conductance is to test if there are some significant ions in the sample were not measured, the equation of CAL was as follows:

$$R_c = \{[H^+] \times 350 + [HCO_3^-] \times 43.6 + 1/2[Ca^{2+}] \times 52.0 + [Cl^-] \times 75.9 + 1/2[Mg^{2+}] \times 46.6 + [K^+] \times 72.0 + [Na^+] \times 48.9 + [NO_3^-] \times 71.0 + 1/2[SO_4^{2-}] \times 73.9 + [NH_4^+] \times 74.5\} / 1000 (\mu S/cm).$$

In Equation (3), $[H^+]$, $[HCO_3^-]$ is to use the measured value.

Table 2 The relationship of the difference of (pH)_m and (OH)_c with I%D

(pH) _m	(OH) _c	I%D	(pH) _m	(pH) _c	I%D
	NADP			Guizhou Province	
4.09	4.07	1.6	5.14	5.16	3.8
4.18	4.07	9.0	3.97	4.67	-9.6
3.93	4.08	-13.1	4.65	5.24	12.33
4.87	7.68	-38.9	4.79	4.63	12.89
4.00	7.53	-45.2	3.75	4.55	-23.9

It is important to notice that the calculated conductance is especially sensitive to $[H^+]$, and the coefficient is 350. This sensitivity makes the comparison of calculated and measured conductance values particularly useful to ferret out bad pH measurement, when the pH is low. For instance, the conductance measured less than 350 ($[H^+]$) may portend that a pH measurement is erroneously low, i. e. the $[H^+]$ is biased high. The conductance percent difference (*C%D*) is calculated with Equation(4).

$$C\%D = \frac{(R_c - R_m)}{R_m} \times 100\%.$$

Table 3 The relationship of the difference of *R_m* and *R_c* with I%D

<i>R_m</i>	<i>R_c</i>	<i>C%D</i>	<i>I%D</i>	<i>R_m</i>	<i>R_c</i>	<i>C%D</i>	<i>I%D</i>
		NADP				Guizhou Province	
39.1	38.9	0.5	1.6	14	13.29	-5.71	3.7
39.1	33.7	-13.9	9.0	91	109.79	20.64	-9.6
6.03	5.5	-8.4	-9.2	25	16.79	-33.2	12.89
60.0	51.5	-14.4	-13.1	38	22.43	-40.97	12.33
15.1	10.8	-28.4	-26.9	84	111.89	33.20	-23.9

From Table 3, it is obviously that the smaller of the percentage difference between the calculated conductance and the measured conductance, the more the *I%D* is near zero, that indicated the cations and anions are in balance.

3 Results and discussion

Upon above equations, the calculation was given to the acid rain data in recent several years

of different months in Guizhou Province of China. Only some results are selected and presented in Table 4.

To these six sets data No. 1 to No. 6 in Table 4, the $I\%D$ less than 20%, the percentage difference ($C\%D$) of R_c and R_m equal or less than 20% portend a good balance. The two sets data No. 7 and No. 8, that $I\%D$ more than 38%, the percentage difference ($C\%D$) of No. 8 is 62%, the origin of such high errors may be complicate. The main reasons are:

(1) Affect of analytical precision and measurement methods

To assure the measurement method standardized and the each measurement reliable, the sample was collected in different time and distributed in extensive range it must have a high level quality assurance to acid precipitation. To reach the aim, it required to control the quality not only in laboratory, but also in fieldwork, i. e. the precision of the system is lower than the instrument precision and laboratory precision for it includes the outside operation and some new changing factors were introduced.

The sample No. 1 to No. 6 in Table 4 have been tested qualified through several times quality - controlled check before measurement, however, sample No. 7 and sample No. 8 have been tested. This could prove that the measuring method and analytical precision are important in measurement.

For sample handling, storing and gathering, CAL take the idea that a great difference of $I\%D$ and $C\%D$ remained between the new samples and no - filtering samples stored in room temperature or under 4°C, for explaining the problems, several groups data from NADP were compared.

Table 4 Ion balance calculation and measurement of Guizhou samples

Sample		Measured concentration											
No.	Month	(pH) _m	[H ⁺] _m	[HCO ₃ ⁻] _m	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	F ⁻	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
1	9	3.94	114.8	0.00	61.4	47.6	8.5	1.6	1.20	6.60	14.5	3.7	8.30
2	6	4.48	33.0	0.156	83.13	19.52	no	no	23.3	4.35	44.0	17.5	10.0
3	6	4.17	67.61	0.08	78.13	8.70	1225.0	0.01	66.9	1.74	33.0	8.3	5.0
4	5	4.08	83.18	0.06	182.9	0.00	101.4	0.0	125.9	5.20	174.4	18.3	15.0
5	9	5.63	2.30	2.24	40.21	3.06	27.32	0.0	10.0	14.78	48.0	28.0	0.00
6	10	5.15	7.10	0.73	23.75	6.71	4.23	0.01	0.0	0.43	30.5	8.3	0.00
7	8	4.88	13.20	0.39	53.33	6.77	7.04	0.01	0.26	1.74	145.0	21.6	0.01
8	7	5.46	3.46	1.49	21.45	2.26	0.56	0.00	7.04	3.05	32.5	22.5	0.00
No.		(pH) _c	Calculated concentration				$I\%D$ Conductance, $\mu S/cm$			$C\%D$			
			[H ⁺] _c	[HCO ₃ ⁻] ₃	A	C	R _m	R _c					
1	4.08	83.2	0.10	117.6	149.1	-11.8	60.3	50.7		-16.0			
2	5.28	5.25	0.98	105.3	132.1	-12.0	26.0	24.8		-4.5			
3	4.86	13.8	0.37	212.1	282.5	-14.0	45.0	54.14		20.3			
4	4.57	26.9	0.19	284.3	422.1	-19.4	65.0	70.69		7.7			
5	5.19	6.46	0.80	70.59	103.4	-18.0	11.0	11.42		3.84			
6	5.93	1.17	4.41	34.75	46.33	-14.3	6.0	7.06		17.2			
7	4.67	21.4	0.24	71.04	181.8	-43.0	10.0	11.95		19.5			
8	5.16	6.92	0.74	28.56	63.55	-38.0	17.0	6.46		-62			

* It is the results calculated by NADP

R (new samples) 5.3, 12.4, 13.0, 36.5, 39.6, 47.8, 50.0, 62.8, 64.5

R (stored samples) 5.7, 15.1, 21.1, 84.0, 60.3, 69.8, 68.6, 98.8, 91.2

If some ions were handled properly before measurement or much weak acid remained in samples, an error must appeared in the value of $C\%D$ and pH. So some more stipulation must be set to the sample - transporting, storing - period, storing temperature and sample - handling.

For the ion balance, that the value of $I\%D$, $C\%D$ must be near to zero through quality - controlled test, the following factors are still considered.

(2) Some significant ions unmeasured existed in sample

Table 4 indicate that the sum of cations is more than sum of anions, $I\%D$ is minus deviation, but the value of $I\%D$ will be becoming small when taking the PO_4^{3-} , oxalic acid, organic acid and some other anions into measurement. From this point, that the poor ion balance of calculation of $I\%D$ perhaps is not resulted from analytical errors, may be exemplified by that some ions were not measured in these samples.

(3) Affect of conductance calculation

A high sensitivity, the coefficient of $[\text{H}^+]$ 350 mentioned in Equation (3), will have great affect on conductance calculation. Measured conductance is higher than calculated conductance portend that value of pH is erroneously high, i. e. $[\text{H}^+]$ is erroneously low. When $C\%D$ is getting higher, we must reanalyze these samples.

(4) Contribution of $[\text{HCO}_3^-]$ to ion balance calculation

Because of the inverse ratio of $[\text{HCO}_3^-]$ and $[\text{H}^+]$, when pH more than 5, the value of $[\text{H}^+]$ is low and the relative $[\text{HCO}_3^-]$ must be high, that must affect the value of $C\%D$ significantly.

(5) The particular of ion balance of precipitation existed in acid rain area of China.

The pH of precipitation in west - southern China is generally less than 5, and the concentration of $[\text{SO}_4^{2-}]$ mostly more than several or tens ppm. If the sample was measured after adding some trace metal and organic alkalic into the solution, the difference of $I\%D$ will be becoming smaller. During measuring the acid precipitation of west - southern China, it is unreasonable only to measure K^+ , Na^+ , Ca^{2+} , Mg^{2+} and NH_4^+ excluding the other trace metal cations such as Fe^{2+} , Fe^{3+} , Mn^{2+} and so on. All these trace metal ions can only be ignored when a high precision of ion balance was unnecessary.

4 Conclusion

Some results were concluded through statistical analysis of ion balance to acid precipitation sample in Guizhou Province of China.

The main method of ion balance evaluation was included in Equation (1). $I\%D$ is not a simple ratio of the sum of cations to anions. It must be noticed that $[\text{HCO}_3^-]$ is excluded from the anions, especially it is very important to the samples of pH 5-7.

It is necessary to measure the ignored significant ions for the poor ion balance. We can properly extend the range of test - criterion of $I\%D$ of ion balance evaluation to the recent year's monitoring item in west - southern China acid rain area in order to reduce the error from unmeasured

ment items.

The Equations (2) and (3) are tenable through comparison among the value of pH, measured conductance and calculated conductance, it also is one of the criterion to evaluated ion balance, especially the value $C\%D$ is an more important criteria. It is important to use the measured error of pH to account for the difference between the measured pH and calculated pH for unknown reasons.

To assure the precision and reliability of $C\%D$, a strict requirement must be set to the sample - transporting, storing - period, storing temperature, and also require a comprehensive test to analytical technique and the analysts.

References

- Peden ME, Campbell SA. Sampling analytical and quality assurance protocols for the National Atmospheric Deposition Program, sampling and analysis of rain, ASTM STP. 1983;72
- Taylor. Quality assurance for environmental measurements, ASTM STP. 1985;867

(Received December 9, 1994)