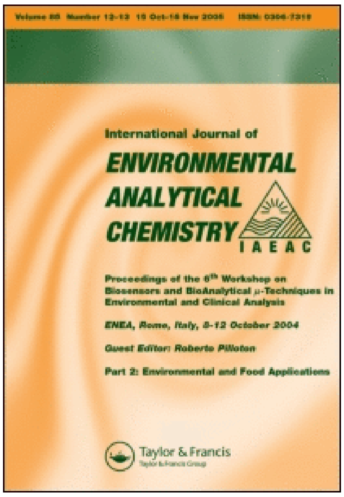

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Reliability and comparability - crucial aspects of research on atmospheric precipitation

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Reliability and comparability – crucial aspects of research on atmospheric precipitation

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The paper presents some research problems concerning the use of different methodologies, particularly focusing on reliability and comparability based on the authors' own research and some literature. The differences involving such factors as the place, mode and frequency of sampling, kinds of samples taken, duration and method of storage from the time of sampling to the time of analysis, preparation of samples for analysis, and verification and interpretation of the results, were investigated. The most significant changes were observed in precipitation samples obtained as a result of different collecting procedures – both in terms of method and frequency. The differences in concentrations of some ions for the corresponding samples of wet and bulk deposition exceeded 100%. On the other hand, the equalisation of samples and results led to the differences in results reaching 20%. The results of analyses of precipitation samples collected within a certain time sequence (monthly) poured together in amounts proportional to the precipitation events, differed from the figures obtained for samples collected on a daily basis and averaged. The greatest differences were observed in the pH and in concentrations of NH_4^+, SO_4^{2-}, and Ca^{2+}. The changes of the composition of precipitation samples stored at a variety of conditions were also investigated. The greatest changes were observed for NO_3^- NO_2^-, and NH_4^+ concentrations. Changes in pH during storage could even range over 1.6 units, which corresponded to more than a 15-fold difference in H^+ concentrations. Evaluation of analytical methods applied with the verification of the validation parameters has been also presented. Moreover, data verification and interpretation by a different method, e.g. comparing the measured value of conductivity with the calculated one or balancing the determined cations and anions, as well as use of statistics (including chemometric techniques), are presented.

Keywords: atmospheric precipitation; sampling; sample preparation; chemical analysis; data checking and reporting

1. Introduction

Atmospheric precipitation affects the natural environment globally. The results of the analysis of atmospheric precipitation samples significantly influence the assessment of the level of atmospheric pollution. That is why the interpretation of the results must be based

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on reliable and accurate data. A wide range of research on atmospheric precipitation is carried out in laboratories all over the world, associated in international and state environment monitoring networks and individual units, including scientific research institutions. However, the numerous results of research presented in literature are characterised by different scientific and interpretative values. It is important to plan an experiment in the way that enables minimising errors at each possible stage; starting with the proper sampling, through the sample treatment prior to the analysis and the analysis itself, ending with the verification and interpretation of the obtained result. There is no gradation of importance of any of the stages as negligence may result in obtaining unreliable information concerning the investigated material and may lead to inaccurate conclusions. Moreover, only the use of analogous research procedures enables the comparison of the research results with literature data.

There are a number of reference studies [1–4] which minutely describe procedures for atmospheric precipitation research. There are also some scientific studies describing the problems of the research on atmospheric precipitation, which include discussions on sampling [5–9] or analytics [5,10–13]. Unfortunately, in spite of the existence of standard manuals, scientific research institutions and some monitoring networks still use their own procedures or they do not meet the requirements of Good Laboratory Practice (GLP), which results in obtaining data of small interpretative value. That is why standard procedures are worth using, keeping in mind that quality assurance/control (QA/QC) and testing are essential.

This study discusses some research problems concerning the use of different methodologies, particularly focusing on reliability and comparability based on the authors' own research and some literature.

2. Experimental

2.1 *Sampling – sitting criteria, collector, sampling period*

The basic aspect in conducting an experiment is a correct sampler location, which assures the representativeness of the collected sample. The initial research should be conducted in the multi-point mode for an investigated area and then, after verification, in the case when statistically significant differences for a given area have not been stated, the single-point mode may be applied in the research.

In order to meet the requirements concerning the sampler location, an area isolated from the direct sources of pollution (unless the pollution from such sources is the subject of the research) and a proper distance from high objects are required. Furthermore, the collector should be situated at a proper altitude [1,2]. The samplers often situated on roofs of buildings do not meet these requirements [14]. The influence of the collector position on the result of physico-chemical analysis of a precipitation sample varies depending on the determined parameter [15,16]. Experiments conducted in Belgium have shown that samples collected from two sites at different heights and separated by a 1 km distance differ in ion deposition by up to 5% [15]. An extensive description of samplers used in the research on atmospheric precipitation has been presented by Krupa [5] and Skarżyńska [9].

Regardless of whether a self-made collector or one commercially available is used, the material it is made of and its construction are equally important. Collecting the precipitation samples into the plastic vessels, e.g. polyethylene, is recommended in determination of anions and cations [1–3]. For the determination of metals and mercury, other materials – glass or Teflon, are required [2,17,18]. The collectors should be chemically inert and maintainable [1–3]. They should also have a sufficiently large collecting surface, which enables collecting small amounts of precipitation [2]. The sampler construction should also minimise the influence of external factors (e.g. wind), as well as reduce sample vaporisation [19,20]. For collecting rain samples, open vessels are often used; however, as the research shows [21], such collectors must be equipped with a side rim, which prevents raindrops from spattering. The authors' own research has shown the differences of up to 30% in the amount of precipitation collected to the funnel ($0.25\,m^2$ and 30 cm rim) with a collecting surface of $1\,m^2$ without rim. Moreover, the collector should be equipped with a narrow mouth collecting vessel to prevent evaporation and concentration of the sample [2], which causes overestimation of the analytes concentration and of the calculated deposition [22]. In order to eliminate the error resulting from evaporation, the special factor is sometimes used. The load differences between monthly precipitation without evaporation correction and weighed mean with evaporation correction amount even to $20\,kg\,ha^{-1}$ for S–SO_4 and N–NH_4, $10\,kg\,ha^{-1}$ for N–NO_3, Cl, K and Ca and almost $4\,kg\,ha^{-1}$ for Mg [21]. The examples of the differences of up to 20% and more in the calculation of deposited acidity, caused by the underrated precipitation amount resulting from external factors like wind speed and height above ground surface, are given by Rodda *et al.* [23].

Another important parameter for the obtained reliable and comparable results is the frequency of collecting samples. The cases of collecting samples within certain time and quantity sequences or on a continuous basis are known [24–26]. Standard manuals recommend the collection of daily samples, or, alternatively, the collection of weekly samples [1–3]. Monthly samples are not recommended [1]. In spite of this, some of the atmospheric precipitation research is based on a system of monthly collection. They are obtained by pouring together daily samples (proportionally to the volume) [27]. The authors of this paper conducted the example research on the influence of the sample collection period on the analytical result. Samples of precipitation collected on a daily basis for the period of a whole month were analysed. At the same time, subsamples from consecutive precipitation events were poured together (proportionally to the volume) and analysed. The results of one experiment are shown in Table 1.

The first part of the table presents the results of the analysis of each single precipitation event. Then weighted mean calculated from the analyses of samples collected on a daily basis. The last line presents the measured result for the monthly sample (poured together proportionally to the volume). The results of the analysis for the sample collected on a monthly basis differ from the monthly mean values obtained from the daily samples. The largest differences observed in this experiment were recorded for pH (H^+), and also for NH_4^+, SO_4^{2-}, and Ca^{2+}. Krupa and Nosal [24], during their research on precipitation samples collected on a daily and weekly basis, stated the largest differences for ions NO_3^- and Cl^-, while Sisterson [28] observed various changes in average concentrations of H^+, NH_4^+ and SO_4^{2-} as well as other compounds, depending on the season of the year.

One should remember that, as the sampling periods lengthens and the time between collection and analysis increases, the potential sample deterioration also increases [1]. Such methodology may be the source of incorrect results because a sample which is left in field for a period of a few weeks is subjected to various physical, chemical and biological changes [29]. It is also noteworthy that by lengthening the collection time, detailed information concerning, for example, the observation of extreme concentrations of analytes, which is of particular significance for ecosystems, may be lost. The influence of

Table 1. Ion concentration (mg L^{-1}), pH, γ – conductivity (µS cm^{-1}) and h – precipitation height (mm) in atmospheric precipitation samples collected on a daily basis (24 h) and a monthly basis (monthly) – poured together in proportion to the volume; samples collected during one month in Poznań metropolitan area (western Poland).

Type	Result	F^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	pH	γ	h
24 h	measured	0.05	1.61	0.05	5.05	5.17	0.47	2.29	0.36	0.20	2.52	5.52	39.6	5.2
	measured	0.02	3.47	0.01	3.62	1.89	0.38	0.87	0.19	0.10	1.28	4.20	36.2	3.8
	measured	0.18	10.07	0.07	10.36	15.09	2.10	8.60	0.65	0.48	6.03	5.61	116.6	0.9
	measured	0.16	10.45	0.15	11.55	14.34	3.97	4.65	0.57	0.35	8.29	5.30	110.2	2.3
monthly	calculated weighted mean	0.07	4.47	0.05	6.21	6.59	1.22	2.74	0.37	0.22	3.48	4.66	57.4	3.0
monthly poured	measured	0.06	4.93	0.03	6.27	7.04	1.70	3.13	0.33	0.26	4.38	6.02	54.6	3.0

Table 2. Concentration of ions ($mg\,L^{-1}$), pH and γ-conductivity ($\mu S\,cm^{-1}$) for the 5 selected samples of bulk and wet only precipitation collected in Wielkopolski National Park (western Poland).

		F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	pH	γ
1	bulk	0.07	2.16	5.05	7.97	0.87	1.27	0.17	0.69	5.70	4.41	58.8
	wet only	0.01	0.51	1.30	1.29	0.29	0.21	0.03	0.18	1.76	5.45	16.5
2	bulk	0.13	3.62	9.20	13.68	1.18	0.92	0.22	1.16	10.20	4.38	96.0
	wet only	0.02	0.74	6.73	4.39	0.27	0.44	0.02	0.40	6.69	5.89	49.1
3	bulk	0.01	0.82	1.75	2.04	0.43	0.12	0.12	0.90	1.65	4.44	25.8
	wet only	0.01	0.50	1.38	1.77	0.18	0.04	0.10	0.77	1.35	4.50	25.6
4	bulk	0.11	3.28	6.85	11.80	1.48	0.38	0.42	1.89	6.13	3.55	109.5
	wet only	0.10	0.48	4.49	1.85	0.55	0.26	0.06	0.58	2.39	4.01	35.1
5	bulk	0.08	2.85	3.22	12.30	0.84	0.32	0.21	1.72	1.82	3.45	149.0
	wet only	0.06	0.59	2.16	1.46	0.43	0.20	0.06	0.53	0.66	4.10	33.4

the precipitation sample collection on the result of physico-chemical analysis has also been described by Losno [6] and Walna [30].

The type of the collected sample depends on the objectives of the researcher. For example, it is possible to collect wet only or bulk (influenced by dry deposition) precipitation samples [15,25,31,32]. The authors' own research on parallel study of bulk and wet only samples showed higher conductivity values (up to 78%) and lower pH (even up to 1.5 units) for the bulk samples. On the other hand, the differences in the concentrations of particular ions exceeded 100%. The detailed results for bulk and wet only samples from five selected precipitation events are shown in Table 2. Other research [19] shows that the contribution of the wet only contribution to bulk deposition reaches between 37 and 125.

The differences between the bulk and wet samples depend on the period between atmospheric events as well as on the meteorological/synoptic characteristics. Moreover, the differentiation in terms of location of measuring stations is observed.

Summing up, one should take into consideration that sampling incorrectness may result in systematic errors which affect the final result of the experiment [33,34].

2.2 *Sample preparation – transport, handling in the laboratory*

The specific character of atmospheric precipitation samples of unstable composition, low ionic strength, burdened with the presence of microorganisms, make those samples an exceptionally difficult material to analyse [5,10]. What happens to the sample from the moment of its collection to the time of the physico-chemical analyses particularly contributes to the uncertainty of an analytical result. These procedures are often not treated with due attention.

A sample from the field should be taken to the laboratory, as soon as possible in a proper vessel (if it is possible, avoid pouring) and kept cool [1–3]. After the measurement of the amount of precipitation (field or laboratory), a sample should be divided into subsamples for physical and chemical analyses. The performed analyses require different procedures of sample preparation. The pH and conductivity determination is performed on an unfiltered sample. However, in order to determine the chemical composition, the sample requires filtration.

The filtration of the precipitation sample is usually carried out with the use of chemically inert filters with the pore diameter of 0.2 or 0.45 µm. The procedure should be done immediately after collecting the precipitation sample because storing a filtered sample prevents chemical substances from dissolving or co-precipitation. The process of filtration also leads to the partial removal of microorganisms from the sample [35]. The authors' own research [30] on four most frequently used filtrating materials (nitrocellulose – NC, cellulose octane – OC, regenerated cellulose – RC, and polyethylosulfonate – PES) of different pore diameters (0.2 and 0.45 µm) shows that, after conditioning the filter (rejecting the first 30 mL of deionised water for 5 cm diameter-filters), filtrating does not influence the chemical composition of the sample. However, in the cold season of the year or in the period of intensive vegetation, the filters were quickly clogged by inorganic and organic matter (for the volume of above 25 mL). The research on using injection filters (*minisart*) of regenerated cellulose (RC) and cellulose octane (OC) has also been conducted. The necessity to reject the first portion of eluent was also noticed here. No differences between filtrating materials with pore diameters of 0.2 µm and 0.45 µm were observed, both for filtered water and precipitation samples (up to 25 mL filtrate).

It is advisable to analyse the sample immediately after it has been transported to the laboratory. However, the sample is often stored. The manuals do not describe precisely the storage time – they only advise on the shortest time possible and also recommend cooling the sample to the temperature of 4°C, or adding biocide [1–3]. The authors' research [30] referred to 12 samples of snow and rain. Both filtered and unfiltered samples were stored in polyetylene vessels, in different temperatures (−4°C, 4°C, ambient temperature), with or without light, for the period of 30 days. Changes in pH, conductivity and concentration of particular analytes were observed.

The pH values change in different ways, even in the same sample storing conditions (Figure 1). The highest increase of pH was observed during the first days (~5 days) from the moment of the sample collection, while after a certain time, which is characteristic for

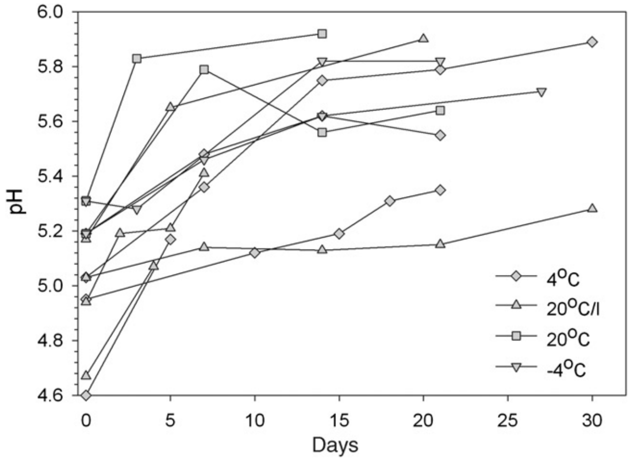

Figure 1. pH changes during the storage of the atmospheric precipitation samples (l – with light, the remaining samples – no light).

each sample, the pH stabilised. Statistically significant pH changes in time ($p \leq 0.05$) indicate that none of the selected storage methods ensures stability of this parameter. The differences ranged even over 1.6 units, which corresponds to more than a 15-fold difference in H^+ concentrations. That is why the measurement of the pH of the sample should be done immediately or a few hours after the collection of the sample. Walna *et al.* [36] and Krupa [5] observed similar changes in their studies. However, some literature sources inform [37] that pH does not change for six days from the time of the sample collection, and only after this time does the pH value start growing. Manuals recommend the pH determination within 48 h [1]. The conducted research on conductivity of atmospheric precipitation did not show any significant changes, regardless of the way the samples were stored. For most samples the changes in conductivity did not exceed ±5%. In two cases (out of 12), the change of 7% and 9% was recorded. It may be stated that the measurement of the samples conductivity may be taken even several days after they were collected [30]. The same 12 samples were also subjected to the chemical analyses (repeated every seven days). The results showed [38] that the smallest changes of concentration were recorded for the magnesium and fluoride ions (less than 10%). Relatively small changes (10–15%) were recorded for the calcium and sodium ions, while significant changes were observed for the chloride, sulphate and potassium ions (20–40%). It seems interesting that both the concentration of SO_4^{2-} and Cl^- showed a growing tendency along with the lengthening of the storing time, while the concentration of K^+ ions either decreased or increased. Statistically significant ($p \leq 0.05$) concentration changes were also observed for the NO_2^-, NO_3^-, NH_4^+ ions. The changes reached 40% for NH_4^+ (mainly the increase of concentration), 30% for NO_3^- (mainly the decrease of concentration) and even 100% for NO_2^- (always the decrease of concentration), especially for those stored in the ambient temperature, both with and without light, and in a frozen samples. A selected example of changes of nitrogen forms in precipitation sample is presented in Figure 2. Similar conclusions concerning the observation of changes in concentration of inorganic nitrogen forms in time were presented by Keene *et al.* [39].

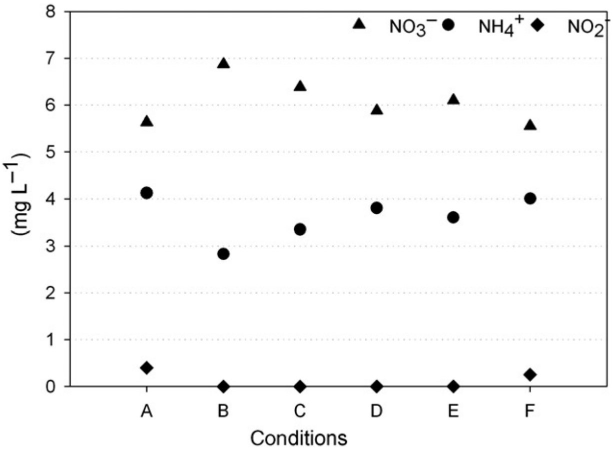

Figure 2. Changes of NO_2^-, NO_3^-, NH_4^+ ions concentration in precipitation samples after a 3 week storage time in different conditions: A – analysis immediately after the collection of the samples, B – temperature 20°C, with light, C – temperature 20°C, without light, D – temperature 4°C, without light, E – temperature −4°C, without light, F – temperature 4°C, with $CHCl_3$.

Inorganic nitrogen forms are particularly sensitive to the changes. That is why the research on the influence of biocide was performed [38]. The samples were preserved by adding $CHCl_3$ in the ratio of 1 mL to 1 L of precipitation. The comparison of the results of the analyses performed one week after the experiment enabled observing the differences of ions concentration which did not exceed 5% for all nitrogen forms. After three weeks, the differences in results for nitrogen oxidised forms increased to 20%, while the concentration of NO_2^- fell below the limit of detection of the analytical technique used. The discussion concerning the changes in NO_2^- and NO_3^- anions concentration in atmospheric precipitation, also for fixed samples, was presented in the paper by Ferrari *et al.* [40]. Summing up, it may be stated that the slightest changes in the concentration of analyte (excluding NO_2^-) in time were observed in the samples stored in the temperature of 4°C, without light, 5–7 days since the collection of a fresh atmospheric precipitation sample. The chemical analysis aiming at determination of the NO_2^- must be performed within a period of several hours from the collection of the sample or the sample should be preserved and analysed within a period of several dozen hours.

Also the type of vessels used for storing the samples should be assessed [38]. The authors inspected the commercially available, new polyetylene sterile and unsterilised vessels (100 mL volume) used in the study. The vessels were rinsed with deionised water (batches of 15 mL each), which then underwent a chromatographic analysis. The results of the research showed that the method of sterilisation used by the producer leaves some ionic chemical substances in the vessel, the presence of which was observed on the chromatogram in the shape of small, unidentified peaks. The analysis of the second portion of water used for rinsing the vessel did not show the presence of these substances. It was assumed, that after rinsing, the vessels were ready for use and could be used for sample storage. The possible influence of adsorption of analytes on the vessel surface or desorption during storage is difficult to assess due to the low ionic strength, instable composition and the presence of microorganisms. One should remember that if the analytical procedure aims at determining the concentration of other chemical compounds (for example, Hg and other heavy metals, especially organic compounds), the required procedures should be used and verified [1–3,41].

2.3 *Sample analysis*

The precipitation samples are analysed with the use of different analytical methods. However, a main obstacle is often the volume of the collected sample being too small, or the concentration of analytes in the precipitation samples being too low.

The most recommended methods used in the analysis of the basic chemical composition are ion chromatography and atomic absorption spectrometry [1–3]. However, it is possible to use titration, potentiometric, spectrophotometric or other methods. The research on the pH and conductivity should involve studies on solutions of low ion strength (appropriate electrodes, special buffer solutions of low ion strength for calibration) [2,11]. The determination of other analytes (for example, Hg and heavy metals or organic compounds) requires using a proper procedure for each analytical method [42,43].

Depending on the determined parameter, and regardless of the used methodology, obtaining good quality and reliable analytical results is the most important aim. That is why the standard methods are worth using in the research, provided they have been previously validated in laboratory conditions. On the other hand, the non-standard

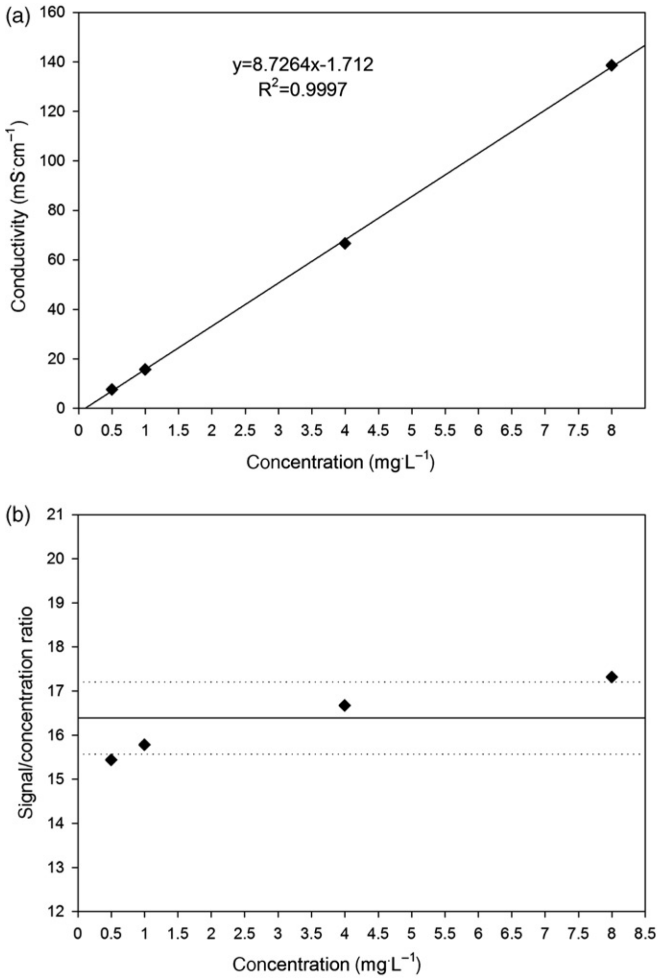

Figure 3. Determination of linearity: calibration curve method (a), and constant response method (b) – determination of NO_3^- by ion chromatography with conductometric detection.

methods must undergo full validation [44]. The evaluation of analytical parameters of measuring procedure (working range, linearity, sensitivity, detection and quantification limits) as well as defining the characteristic features of the obtained result (traceability, uncertainty: recovery, robustness, repeatability, reproducibility) may be included in the most important elements of the validation procedure [45].

In order to determine the working range, linearity and sensitivity, the calibration curve (e.g. three repetitions for six concentration levels) of measuring device is used in the range that involves the expected value. The regression parameters are then evaluated (Figure 3a). However, determining the constant response range of the detector is more reliable (Figure 3b).

The points (corresponding with the concentrations of standard solutions) lying outside the probable error margin (e.g. ±5%) correspond with the analyte concentrations outside the linearity range of the measuring device.

Table 3. Results of analysis of the certificate reference material (CRM) – RAIN 97, with the use of ion chromatography method.

Analytes [mg L^{-1}]	CRM	Measurements
Cl^-	0.53 ± 0.09	0.54 ± 0.01
NO_3^-	9.21 ± 0.16	9.60 ± 0.38
SO_4^{2-}	5.28 ± 0.73	5.79 ± 0.33
Na^+	0.28 ± 0.04	0.30 ± 0.02
NH_4^+	0.23 ± 0.03	0.25 ± 0.01
K^+	0.15 ± 0.04	0.16 ± 0.01
Mg^{2+}	0.93 ± 0.09	0.98 ± 0.01
Ca^{2+}	2.64 ± 0.25	2.91 ± 0.05

In the evaluation of the working range, the precision and accuracy of measurements should also be considered. The precision is defined based on the RSD calculation or by the comparison with the reference method (the comparison of two values of standard deviation – Snedecor's Test). The accuracy may be defined according to various procedures. However, the best method involves conducting the certificate reference material analysis (e.g. RAIN 97) and evaluating it using the Student's *t* Test (Table 3).

The overlapping ranges for certificated and measured value indicate that the suggested methodology complies with the accuracy condition. The statistical procedure in accordance with Student's *t* Test was also used. For example, the critical value (t_{cr}) of 2.57 ($\alpha = 0.95, f = 5$) was determined, and then the Student's *t* Test parameter value was calculated for the measurements results. For Cl^- ions t was 2.45, and therefore it may be stated that the determined concentration value does not significantly differ in terms of statistics from the certificated value ($t \leq t_{cr}$) [46].

In the case of the research on atmospheric precipitation, the determination of limit of detection (LOD) and limit of quantification (LOQ) is also crucial due to frequent determinations of low analyte concentrations. The way of determining the limits depends on the nature of analytical method, the characteristics of applied instrumental technique and on the possibility of obtaining so-called 'blank samples'. The determination is also conducted differently for different methods [47]. One should remember to check the correctness of the determined values. For example, for chromatographic methods, the limits of detection and determination may be stated using the interrelation of the analytical signal ratio (S) with the average level of background noise (N) for a given pattern – S/N. The three-fold value of noise is assumed as the detection limit, while the three-fold value of LOD is the limit of quantification. The noise level is determined for a 'blank sample', for the retention time corresponding with the retention time of the ion for which the limit is determined [38].

As was already mentioned, the traceability is necessary for obtaining reliable results. The traceability is ensured by the correct results of the analysis of certificated reference material (Table 3). On the other hand, calculation of uncertainty budget, although sophisticated, is recommended because it encompasses all factors which may affect the uncertainty of the result [44,47–50]. The factors differ depending on the analytical methods applied. However, according to the *Guide to the Expression of Uncertainty in*

Measurements [51], in order to determine the uncertainty of the analysis result, the following conditions must be fulfilled:

- the measurements procedure for the measurand must be defined;
- modelling (usually mathematical) must be applied to calculate the analysis result based on the measured parameters;
- the values must be assigned to all the possible parameters that could affect the final result of the analysis, and the standard uncertainty for each of them must be determined;
- the applied principles of uncertainty propagation in calculating the standard uncertainty of analytical result;
- presentation of the final result of the analysis as: result ± expanded uncertainty (after using an appropriate factor).

Bear in mind that obtaining the reliable results of analytical measurements requires not only the use of the control system and ensuring the quality of the obtained results (QC/QA), but also their evaluation – testing.

It is worth conducting periodically the analysis of control samples, the certificate reference materials (e.g. Table 3), the blank and spiked samples [52], as well as comparison of the results achieved with reference method [52] or participate in inter-laboratory comparison [49].

2.4 *Data checking and reporting*

A great number of collected results and their complexity forces the researchers to use graphical and statistical techniques to verify the data.

The first part of the data checking procedure is to monitor errors. Random errors – the outlier values – may be determined with the help of statistical tests (e.g. Dixon's Q Test). However, it should be noticed that the presence of a high concentration of analytes may indicate unique natural conditions, and not necessarily an analytical error (e.g. gross) [45]. For example, the result of chemical analyses of precipitation samples collected on 28 and 29 June 2003 in a city agglomeration shows a high concentration of NO_3^- and SO_4^{2-} ions up to 12 and 14 $mg\,L^{-1}$ and 13 and 13 $mg\,L^{-1}$, respectively. Three-fold higher value of the annual mean resulted from local pollution [53].

The systematic errors verification may be conducted based on the comparison of accuracy of two procedures (mean values). Initially, the procedures are compared with respect to precision (Snedecor's F Test). If the compared methods do not differ in terms of statistics, their accuracy is compared using the Student's t Test. If the compared procedures differ statistically and significantly with respect to precision, their accuracy is compared using approximate Ochran-Cox C Test (for poor/small result series) or Aspin Welch Test [47].

It is also noteworthy that a detailed laboratory log is very helpful for data checking and verification as in many cases the results that are far from expected are caused by external conditions (e.g. bird droppings or sampler damage). A detailed description of conditions and observations during a precipitation event is also valuable.

The ways of assessing the correctness of the performed chemical analyses involve comparing the measured value of conductivity with the calculated one [2,3] or balancing the determined cations and anions (which is possible once we perform a full chemical analysis). The description of different expressions of ion and conductivity balances was presented by Plaisance *et al.* [54]. It should also be stressed that in the solutions of such a low content of mineral substances balancing of cations and anions may differ up to 60% (sum of ions $\leq 50\,\mu e\,L^{-1}$) [1].

Presenting the results might be also complicated due to their aforementioned accumulation and complexity. In the atmospheric precipitation study basic statistical parameters describing the distribution of particular variables are used. These include: mean, minimum and maximum values, median, standard deviation and skewness. Studies often lack information on the method of determining the mean value. Sometimes, the arithmetic mean is used, while this value may only be used for a normal distribution of data (in such cases the set skewness value should also be presented). In the atmospheric precipitation studies the weighted mean is especially recommended since it not only conveys the information concerning the average analyte concentration in a sample, but also includes the amount of precipitation.

Moreover, data reporting can be done with the use of chemometric techniques [55,56]. Application of various multivariate approaches for interpretation of these complex data matrices offers a better understanding of environmental quality and ecological status of the studied system. The most frequently used techniques include: the Principal Component Analysis (transforms a number of possibly correlated variables into a smaller number of uncorrelated variables – principal components), the Time Series Analysis (accounts for the fact that data points taken over time may have an internal structure such as autocorrelation, trend or seasonal variation), the Correlation Analysis (indicates indirect relationships in survey data), the Discriminant Analysis (used to determine which variables discriminate between two or more naturally occurring groups), and the Analysis of Variance (observed variance is partitioned into components due to different explanatory variables) – ANOVA. The use of chemometric techniques in the interpretation of the results of the atmospheric precipitation research was presented in the authors' own papers

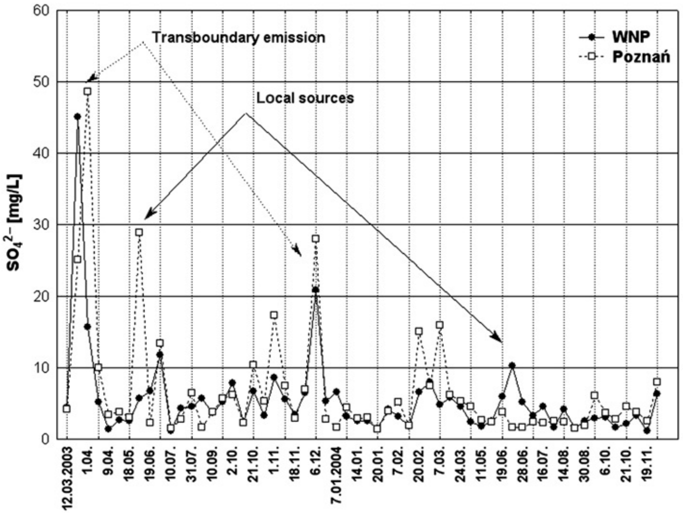

Figure 4. Time sequence of per event sulphate concentrations in atmospheric precipitation samples from March 2003 to November 2004 recorded in Wielkopolski National Park (WNP) and Poznań metropolitan area (western Poland).

[55,57,58] and others' work [56,59]. The examples of time sequence of per event sulphate concentrations (Figure 4), results of PCA analysis (loading plots) (Figure 5) and the ANOVA results with accordance to the category obtained by wind characteristics (Figure 6) for results of precipitation samples collected in metropolitan area and protected woodland in the vicinity has been presented [55,57,58].

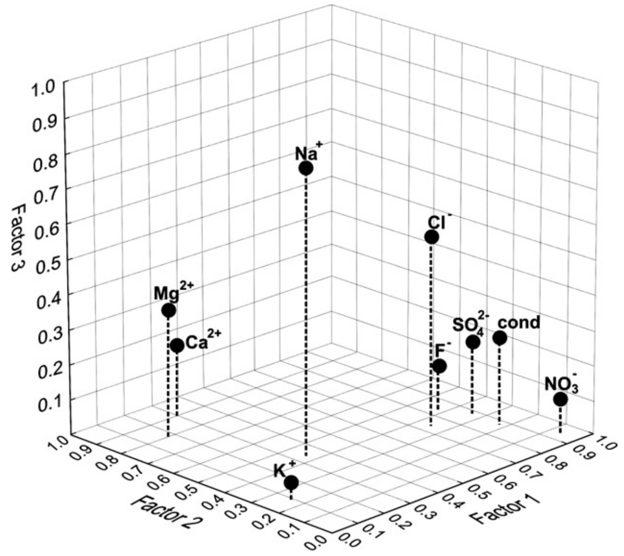

Figure 5. Results of PCA analysis (loading plots) for precipitation samples collected in Poznań metropolitan area (varimax normalised rotation).

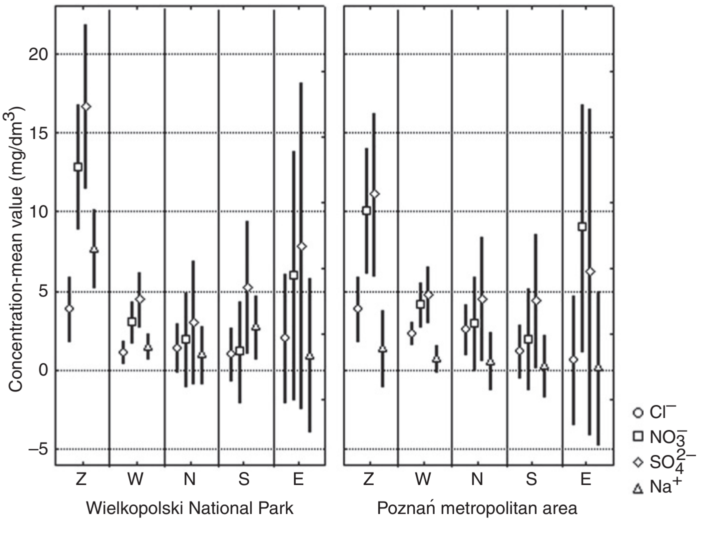

Figure 6. The ANOVA results with accordance to the category obtained by wind characteristics analysis (Z – changeable, W – west, N – north, S – south, E – east), horizontal lines represent dispersion value. Precipitation samples collected in western Poland (Wielkopolski National Park and Poznań metropolitan area).

It is also noteworthy that in the assessment of the level of atmospheric pollution one should consider its background, i.e. the level of the concentration of analytes present in the precipitation on the level characteristic for the environment without pressure. In order to do so, the use of the results of the research conducted by international network, e.g. the European Background Monitoring Network (EMEP), is recommended [60,61].

For the same reason, when analysing the research results of atmospheric precipitation located near the sea, the naturally increased content of sea aerosol ions should be taken into consideration [2,62].

It should be also highlighted that comparing the results obtained by different research procedures may cause some mistakes in the interpretation of the results and in drawing conclusions.

3. Conclusion

As has been demonstrated, a reliable result of atmospheric precipitation studies is affected by all the stages of applied procedure. Each stage is equally important and requires special attention. Quality assurance, control (QA/QC) and testing during all experiments are essential for obtaining a reliable data.

Moreover, a result of a chemical analysis of precipitation may be compared with other results only when an adequate procedure is used. Therefore, standardised methods are recommended and a detailed description of the used research procedures should be described in every paper.

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