Rapid evaluation of ammonium in different rain events minimizing needed volume by a cost-effective and sustainable PDMS supported solid sensor[☆]

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ABSTRACT

The presence of ammonium ion in rainwater is due to atmospheric processes which involve its scavenging from gas phase and particulate matter. The fractionated samplings of rainwater can provide information about these processes and their potential sources. However, only a low sample volume may be available, which constrained the analysis in general and more particularly in situ mode. For minimizing this limitation, this work proposes a polydimethylsiloxane (PDMS)-salicylate sensor that produces a color change. The embedding of solid reagents into PDMS was optimized. Good analytical characteristics (analysis time of 10 min, sample volume of 500 μL, limit of detection 0.03 μgmL^{-1}) were obtained. Furthermore, other features of the method such as carbon footprint, equipment cost, residues, toxicity and safety have to be taken into account to be assessed according to the Green Analytical Chemistry approach. In this sense, the hexagon tool was employed for comparing the proposed sensor with methods based on the same reaction as well as with general methods for the ammonium analysis in water (using luminol, ion selective electrode, Nessler and modified Roth method). The proposed method based on PDMS-salicylate sensor stands out from all the others by its sustainability, particularly, in terms of low carbon footprint, residues and cost. The method was applied to fractionated samplings in a suburban site (Galicia, Northwestern Spain) and a higher contribution of the rainout process was observed. When long-duration rain events were analyzed, a relationship between the sampling time and ammonium concentration could indicate a loss of ammonium ion over time.

The research focuses on developing an innovative PDMS-sensor, for monitoring ammonium determination in rainwater under wide conditions (scavenging process).

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1. Introduction

Ammonium and ammonia are found in the atmosphere in several matrices (gas phase, particulate matter, and rainwater). Ammonium neutralizes the major anions such as sulfate, nitrate and chloride. The incorporation of ammonium to rainwater, as occurs with other pollutants, is the consequence of scavenging ammonia in gas phase or ammonium in particulate matter (Andronache, 2003; Zheng et al., 2018). When the rain starts, the first fractions sweep pollutants of local atmospheric column below clouds coming from local or regional sources; it is the so-called washout process (Xu et al., 2017; Fernández-Amado et al., 2016, 2017; Lu et al., 2019). In the following fractions, the rain can sweep pollutants which are found in the clouds and which may have been transported from a long distance. This phenomenon is called rainout process (Celle-Jeanton et al., 2009). The ammonium analysis is carried out by sampling over long periods of time or using sequential samplers in which the collected sample volume is lower. For the latter purpose, rapid analysis methods which require low sample volume are necessary.

Monitoring natural processes that take place in the

environmental field can be performed by *in-situ* analysis. In this regard, colorimetric sensors are suitable for this type of analysis, if necessary, as well as providing other characteristics such as simplicity, rapid visualization, sensibility, and cost-effectiveness. Polydimethylsiloxane (PDMS) is a permeable material that can be used as support in *in-situ* devices since the analytes or the reagents can be diffused through PDMS from or to a solution (Seethapathyand Górecki, 2012; Prieto-Blanco et al., 2015, 2019). In the analytical literature, many sensors using new materials and reactions were proposed, but only few of them were assessed depending on their applicability at different matrices and analytical features.

The determination of ammonium by colorimetric reaction can be generally carried out by using the classic Berthelot reaction. It is a two-step reaction (formation of monochloramine and formation of indophenol) and it requires several reagents, some of which are toxic (Searle, 1984; Prieto-Blanco et al., 2015, 2019). But, Berthelot reaction is very versatile thanks to the phenol and it can be changed by several substituted phenols, leading to the formation of indophenols. Among them, there is sodium salicylate (SL), however its reactivity is lower than that of phenol due to the carboxyl group. Thus, the reaction time is very long (60 min) (Tao et al., 2008, Verdouw et al., 1977). The advantages of SL are related to its solubility in water and lower toxicity. Here, we demonstrated that SL can also provide adequate analysis time when it is embedded in PDMS, changing its reactivity.

On the other hand, the design of sustainable methods takes into account aspects such as time, efficiency, waste, toxicity and analytical features. In this regard, a quantitative evaluation of the new proposed method was carried out from the hexagon tool proposed by the MINTOTA research group (Ballester-Caudet et al., 2019). Five blocks which include figures of merit, toxicity and safety, residues, carbon footprint, and economic costs of the method are considered. Each of these items is assessed with penalty points ranging from 0 to 4. Thereby, it is possible to compare several methods with similar purposes by eye inspection of the penalty points assigned to each item and, eventually, select the most convenient method according to the specific purposes. Several methods for ammonium determination in water analysis are evaluated against the SL sensor by the hexagon tool. The performance of the SL sensor was better compared to those offered by the other methods, even those based on the Berthelot reaction. As a result, the salicylate sensor is proposed for studying the removal of ammonium, coming from several sources, from rainwater.

2. Material and methods

2.1. Instrumentation and reagents

For UV−vis measurements, two spectrophotometers (UV−6300PC-Spectrophotometer; VWR, Belgium and Lambda 6 UV/vis Spectrometer; Perkin& Elmer, USA) and a 10 mm path length quartz microcell with a volume of 700 μL (Hellma Analytics, Germany) were used.

Thymol (99.998%) and ammonium chloride ($\geq$99.9995%) were purchased from Sigma-Aldrich; USA. Other reagents were obtained from different sources: sodium salicylate (min 99%) (Scharlau, Spain), sodium nitroprusside (99.97%) (Probus, Spain), sodium hypochlorite (10%) (Panreac; Spain) and ketone (>99.8%) (Romil, Spain). Sylgard 184 silicon elastomer and Sylgard 184 silicon elastomer curing agent were purchased from Dow Corning, USA. The discs were gelified into polystyrene immunoassay plates by Corning Incorporated, USA.

2.2. Preparation of PDMS-salicylate-nitroprusside (PDMS-SL-NP) and PDMS-thymol-nitroprusside (PDMS-TM-NP)

The PDMS-TM-NP discs were prepared according to Prieto-Blanco et al. (2015), 2019. However, in this work, the dispersion of 26 mg of sodium nitroprusside was performed using a bath with ultrasound. The mixture was mechanically stirred each 10 min (total time of 40 min) to facilitate the dispersion.

The preparation of PDMS-SL-NP was performed adding to the 3 g of elastomer base, the solid reagents (51 mg of SL and 26 mg de NP) which are finely powdered at the moment of the addition. The same agitation process for the PDMS-TM-NP discs was also performed in this case. Then, 0.3 g of curing agent was added and 0.2 g of the homogenized mixture was weighed in each well of the plate. The discs solidified after 2−3 days at room temperature. The dimensions of each disc were 1 cm diameter and 200−1550 μm thickness.

2.3. Derivatization procedure

500 μL of standard solution or samples were mixed with 20 μL of 1 M NaOH and 1.25% NaOCl (for PDMS-TM-NP discs) or 10 μL of 1 M NaOH and 0.6% NaOCl (for PDMS-SL-NP discs) contained in a glass vial. The mixture was manually stirred during 1 min for the monochloramine formation. Then, half disc cut in small pieces was introduced in the solution and maintained 10 min for the indophenol formation. Subsequently, the absorbance was measured.

2.4. Analysis of rainwater samples

Rainwater was collected in a suburban area where the University of ACoruña is located (A Zapateira, A Coruña, Spain). A silanized glass sampler (DEPOBULK®, LabServiceAnalytica, Italy) was used and the obtained samples were filtered through quartz filters of 4.7 cm diameter (Scheicher & Schuell, Germany) and stored at −18 °C until analysis. The sampling periods were April−May 2016, March−April 2017, July 2017 and September−October 2017.

Two kinds of rain events were sampled: short events (lasting less than 16 h) and events lasting more than 20 h in which all the accumulated rainwater had been collected. In the case of the short events, fractionated samplings were performed each 1−3 h.

3. Results and discussion

3.1. Optimization of the preparation of PDMS-SL-NP discs

SL was dispersed as a finely powdered solid in the same way as the NP reagent. The dispersion of reagents was reached using two types of agitation, namely ultrasound bath and mechanical agitation. The former favors the breaking up of the particles, whereas the latter improves homogenization. It is worth mentioning that the temperature reached by the bath (40-54 °C) facilitated the entire process. Using this procedure, six batches of PDMS-SL-NP, with 12 discs each, were prepared. Additionally, PDMS-TM-NP discs were prepared using the above-mentioned combined agitation.

The discs were observed by optical microscope in order to check the dispersion of the reagents. The discs showed a flat base and meniscus around. In the PDMS-TM-NP discs, the embedded reagents were found 150 μm around the front face of disc, in contact with the plate (matt aspect) during the gelification process. This fact indicated that, the reagents were deposited by gravity during the gelation. In PDMS-SL-NP discs, the crystals of nitroprusside can be observed in the discs (see Fig. 1A). A better dispersion of the reagents was observed when the discs were cut in pieces by means of polarized light. 1550 μm thickness in the bottom and 200 μm in
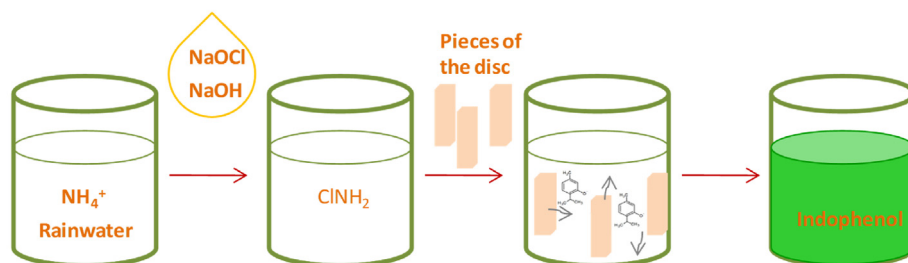
A)
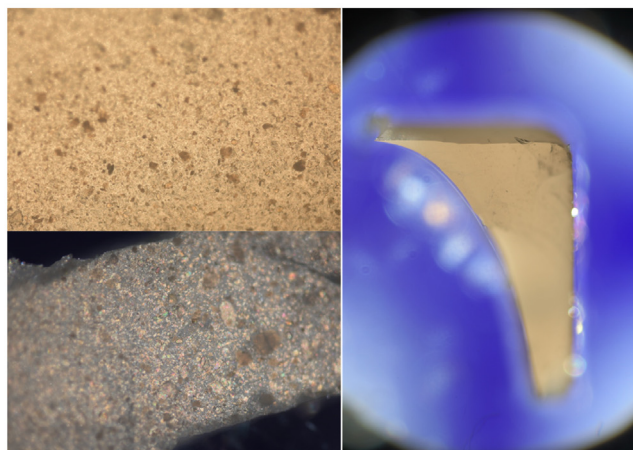
B)

C)

Fig. 1. A. Images of a salicylate disc taken by optic microscope: above, inside of the disc; below, bottom of the disc; right, edge of the disc. The last images were taken by polarized light.. B. Images of the salycilate disc and indophenol solution in quartz microcell. C. Diagram of the working principle.

the edge were obtained (Fig. 1A). For each derivatization, half of a disc cut in eight pieces was used.

The derivatization reaction was tested under optimized conditions for PDMS-TM-NPS, (half a disc, 20 μL of solution containing 1 M NaOH and 1.25% NaOCl). Several volumes of solution (10, 15, 20, 40 μL) were tested. The lower volume, the higher the response. The effect of sodium hydroxide and hypochlorite concentration was studied and it was observed that around 0.6% NaOCl the absorbance was similar to that measured with the thymol discs (Fig. 1S). In the literature it was reported that the excess of sodium hypoclorite with respect to the stoichiometric value could prevent the formation of indophenol due to the blocking of *para* position of the salicylate (Kempers andKok, 1988). Finally, 10 μL of 0.6% NaOCl and half a disc were employed in the derivatization (Fig. 1B).

The working scheme according to Berthelot's reaction is shown in Fig. 1C. Firstly, monochloramine was formed by the reaction between ammonium and hypochlorite/sodium hydroxide solution.

Then, the pieces of a half disc were introduced in the solution and the reagents trapped in the disc (salicylate and nitroprusside) were diffused to the solution making up the colored indophenol.

The PDMS-TM-NP method used the discs prepared according to the new conditions described in section 3.1 and the previously described optimized derivatization conditions (Prieto-Blanco et al., 2015, 2019).

Linearity, limits of detection and limits of quantitation, precision and recoveries are shown in Table 1 for PDMS-SL-NP sensor compared with those achieved by PDMS-TM-NP. LOD and LOQ were calculated as 3 (Sa/b) and 10 (Sa/b), Sa being the standard deviation of intercept and b the slope of calibration curve. The LOQ obtained for the PDMS-SL-NP method was less than 30% of the parametric value (0.5 mg L^{-1}) established by the European Unionfor ammonium in water intended for human consumption (Council Directive 98/83/EC; Commission directive (EU) 2015/1787). The inter-day precision did not have a significant increase when different

Table 1
Analytical characteristics of the two methods using different devices.

Parameter	PDMS-SL-NPS Method	PDMS-TM-NPS Method
$y = a + bx$		
$a \pm s_a$	0.0624 ± 0.0068	0.1114 ± 0.0135
$b \pm s_b$	0.2396 ± 0.0032	0.1656 ± 0.0048
R^2	0.9991	0.9958
LOD (μg/mL, NH_4^+)	0.03	0.08
LOQ (μg/mL, NH_4^+)	0.09	0.3
CV (%)inter days, inter batches,	10.6 (n = 13 and 4 batches)	9.5 (n = 11 and 3 batches)
CV (%)inter day	6.8 (n = 8)	11.0 (n = 6)
CV (%) intra-day	2.2−4.5 (n = 3)	6.4 (n = 3)
Recovery (%)	82 ± 4 (n = 3)	109 ± 13 (n = 3)

batches of discs were considered, especially for the PDMS-TM-NP method. The slope of the calibration curves for the two methods was compared. The variances were comparable since Fexp = 3.1 was lower than Fcritical = 5.05. However, t_{exp} (11.98) $> t_{critical}$ (2.228) for 10 freedom degrees and confidence level was 95%. Therefore, the two slopes showed significant differences. The slope of the PDMS-TM-NP method was 70% of the PDMS-SL-NP method. Control charts were performed for the two methods and all the points were within the control limits (mean ± 2 σand mean ± 3 σ).

Vieira et al., (2013) proposed a method for a flow system based on the Berthelot reaction using salicylate as a reagent. Compared to the PDMS-SL-NP method, the linear range (up to 1.2 μg mL^{-1}) was narrower, there was a higher volume of used reagents and generated waste (3.1 mL per sample), and LOD (0.019 μg mL^{-1}) was comparable.

3.2. Study of different rainwater events

The PDMS-SL-NP method was applied to two different types of samplings (see Material and Methods section). In previous studies, organic pollutants (polycyclic aromatic hydrocarbons and phthalates) were analyzed at trace levels in areas surrounding the city of A Coruña (Galicia, Spain) (Fernández-Amado et al., 2016, 2017). Results showed that the higher the volume of sample collected, the lower the concentration. This fact indicated that the washout process was predominant in the removal of these compounds from the atmosphere. Bertrand et al. (2008) observed a predominance of washout for mayor ions (including ammonium) in Opme, France. However, in the literature there are also reported examples of the predominance of the rainout with respect to the washout process for ammonium, sulfate and nitrate (Gonçalves et al., 2002).

In the present work, the values obtained for ammonium were constant or increasing during the precipitation for events with fractionated samplings (see Table 2). In addition, a positive correlation between the sampled volume and the concentration was found ($R^2 = 0.57$) indicating a greater contribution of rainout process. However, it is necessary to consider as definitive conclusions that the sampling site and the meteorological conditions play an

important role in the predominance of the two processes (Bertrand et al., 2008). For long duration events, (Table 3), no correlation between the sampling volume and the concentration was found. Nevertheless, a strong relationship between the sampling time and the ammonium concentration was observed. That is, for more than 40 h of sampling, the ammonium concentration was about 20 μM (see Fig. 2). Problems of stability of ammonium ion over time could occur.

The average value for short events was 43 ± 20 μM and 49 ± 60 μM for longer events (without including the dew sample). Atthis site, Moreda-Piñeiro et al. (2014) obtained also values of 32.5 μM (CV = 231%) in monthly samples from March 2011 to August 2012. The values found are within the range of those found atother worldwide sites (Rao et al., 2016), although lower than Beijing (345 μM, Xu et al., 2015), Mexico city (95 μM, Baéz et al., 2006) or Thessaloniki, Greece (116 μM, Anatolaki and Tsitouridou, 2009).

3.3. Characterization of the sensor by the hexagon tool

A quantitative evaluation of the sensor performance was carried out using the hexagon tool (Ballester-Caudet et al., 2019). This evaluation tool was applied to assess sustainability, associated risks, analytical features and related costs when using the proposed sensor and other ammonium determinations for water analysis (Molíns-Legua et al., 2006), and the results are summarized in the regular hexagonal pictogram shown in Fig. 3. Each equilateral triangle corresponds to a variable of the evaluated method, namely figures of merit, sustainability estimated through the carbon footprint calculation, generated residues and related cost of the methodology. Particularly, toxicity, hazards and safety considerations are included in the same triangle of the hexagon tool.

As shown in Fig. 3, both PDMS-SL-NP and PDMS-TM-NP sensors offer similar analytical performance, the SL sensor being an improved alternative to the TM sensor (Prieto-Blanco et al., 2015) due to the enhancement of the limit of detection in the figures of merit of the method. When considering additional spectrophotometric methods carried out in solution, it was observed that the

Table 2
Results obtained (ammonium concentration, pH and conductivity) and sampling conditions (volume and time) for fractionated samplings of precipitation events. *A, B and C* correspond to a sequence of sampling.

Sample	[NH_4^+] μM	[NH_4^+] μg/mL	pH	Conductivity (μS/cm)	Volume (mL)	Time (hours)
E160605A	40.0 ± 0.5	0.72 ± 0.01	−	−	7.5	1.3
E160605B	37.3 ± 0.2	0.67 ± 0.01	7.5	60	10.5	0.7
E172303A	< LOQ	< LOQ	6.3	130	90	2.2
E172303B	41.1 ± 2.2	0.74 ± 0.04	5.5	130	50	2.8
E172303C	61.3 ± 2.5	1.10 ± 0.04	6.4	368	70	2.2
E172109A	55.7 ± 0.7	1.0 ± 0.01	6.4	103	50	1.25
E172109B	63.0 ± 3.0	1.13 ± 0.05	6.9	117	46	1.5

Table 3
Results obtained (ammonium concentration, pH and conductivity) and sampling conditions (volume and time) for longer events of precipitation.

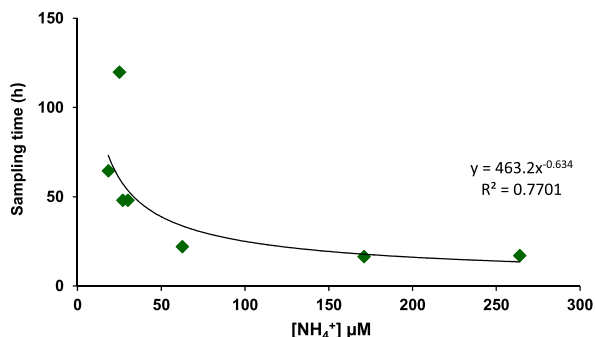| Sample	[NH$_4^+$] μM	[NH$_4^+$] μg/mL	pH	Conductivity (μS/cm)	Volume (mL)	Time (hours)
P161904	< LOQ	< LOQ	7.3	–	37.5	23
P162004	27 ± 2	0.49 ± 0.03	7.9	79	22.5	48
P172303	171 ± 7	1.54 ± 0.06	–	–	430	16.4
P170103	30 ± 1	0.54 ± 0.01	6.8	104	730	48
P171907	25.0 ± 0.4	0.45 ± 0.01	–	–	220	120
P172707	<LOQ	<LOQ	–	–	80	21.5
P171809	18.4 ± 0.1	0.33 ± 0.01	7.1	66	330	64.5
P172010	23.0 ± 1.1	0.41 ± 0.02	6.5	37	90	20
P172604[a]	264 ± 3	4.75 ± 0.06	5.9	44	4	17

[a] Dewsample.

Fig. 2. Relationship between the ammonium concentration and the sampling time for the long duration events.

the indophenol was the least environmentally-friendly due the amount and toxicity of the residues generated. These aspects are improved when considering the indothymol analytical procedure (thymol in solution as a reagent), which additionally guarantees the same sensitivity as in the case of the indophenol method. Despite this fact, figures of merit and the degree of automation are variables that are noticeably improved when moving towards the PDMS-SL/TM-NP sensors. They show adequate sensitivity to determine ammonium in water by means of a direct determination, green and low cost analytical procedure.

In Fig. 4, the hexagon pictogram of the PDMS-SL-NP sensor is compared to that obtained for ammonium determination in water using different analytical techniques. Taking into account the colored reaction, modified Roth's and Nessler methods are the most
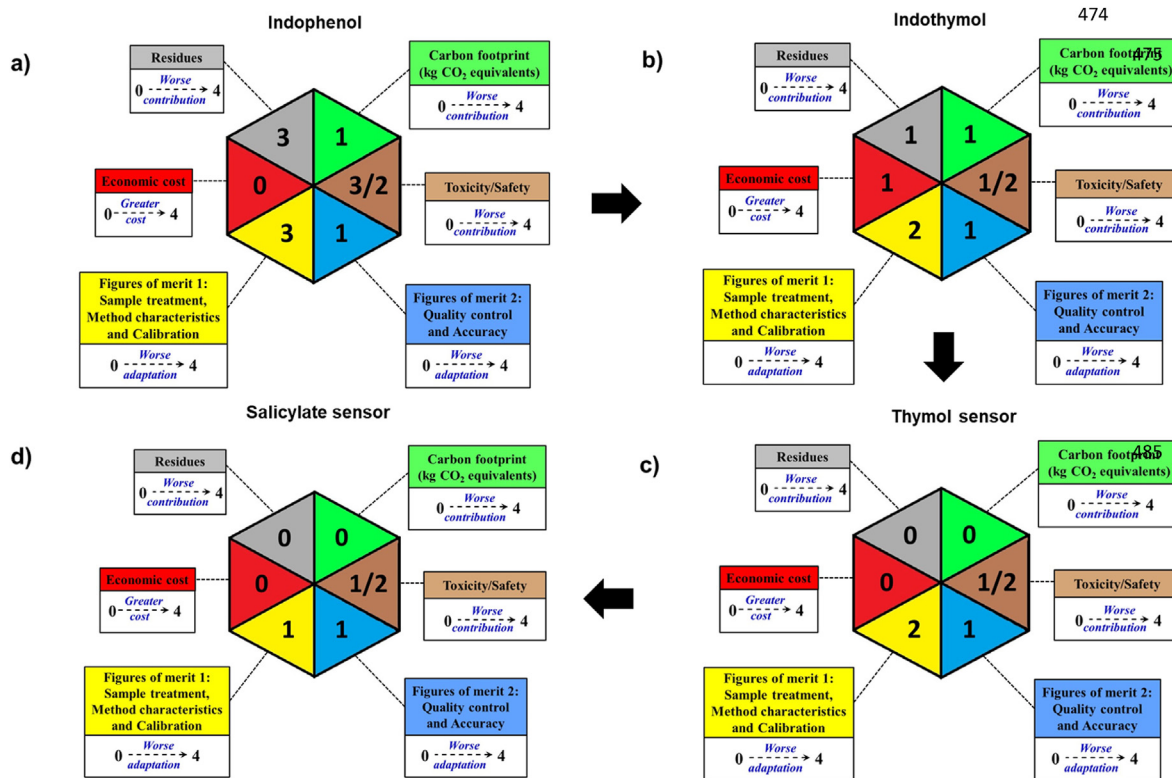

Fig. 3. Regular hexagon pictogram for indophenol (a), indothymol (b), thymol- (c) and salicylate-PDMS-NP (d) sensors for ammonium determination in water using a UV−Visible spectrophotometric technique.

indophenol method and indothymol method had 3 and 2 penalty points associated with toxicity and safety, respectively. Moreover,

selective for ammonium detection compared to the ISE or luminol methods (Molíns-Legua et al., 2006). However, Nessler method
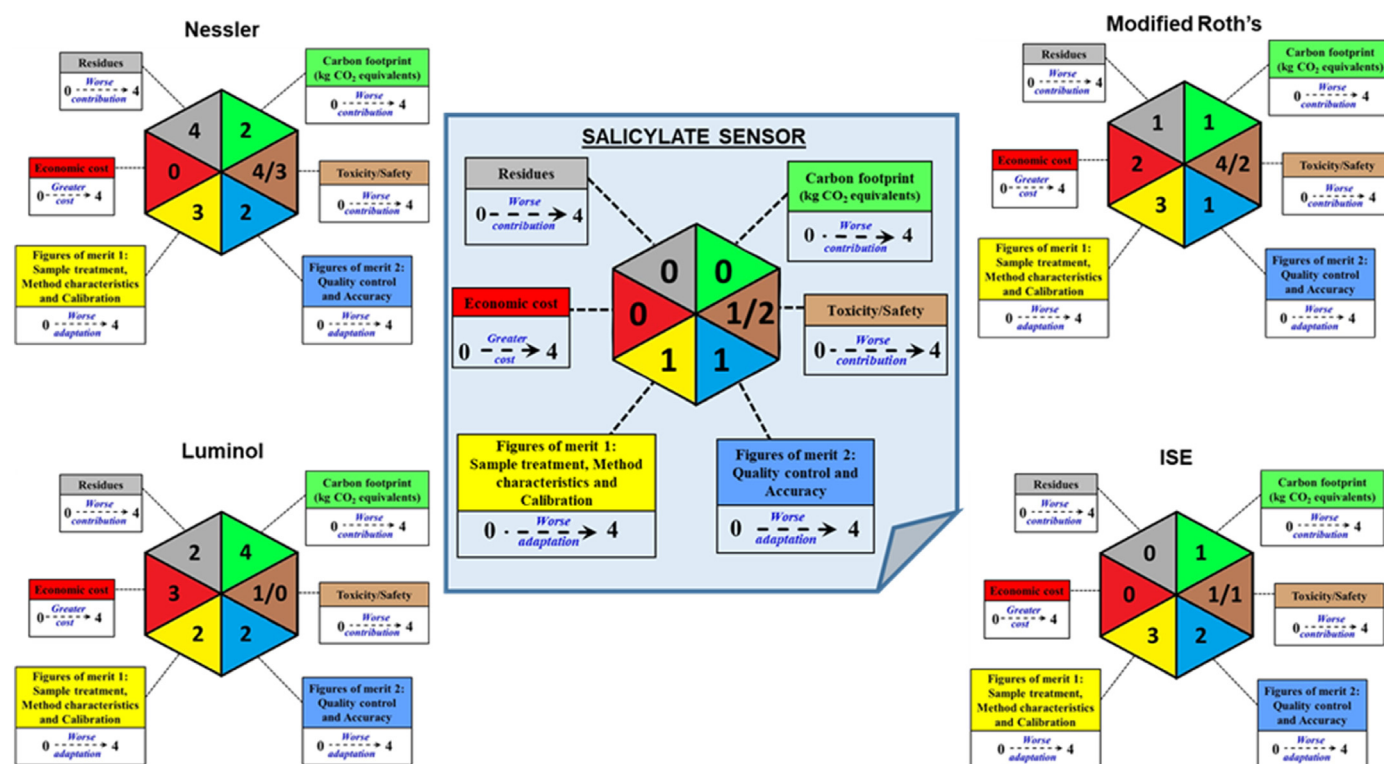
Fig. 4. Comparison of the quantitative evaluation of the PDMS-SL-NP sensor with Nessler (UV−Vis spectrophotometry), Modified Roth's (fluorescence), luminol (quimiolumi-nescence) and ISE (potentiometry) methods for an ammonium analysis in water samples.

requires the use of toxic reagents (4 penalty points), offers inadequate figures of merit (3 penalty points) and shows greater environmental impact (residues and carbon footprint variables) than the PDMS-SL-NP sensor. On the other hand, luminol method provides the least time-consuming analysis, but its high capability of automation increases the cost of instrumentation, being the most expensive option among all the methods considered in Fig. 4. Moreover, the luminol method involves the most negative environmental impact since the energy consumption of the instrumentation takes into account a flow-injection system. In the case of the ion selective electrode (ISE) method, potential measurements by means of electrodes imply an analytical procedure with the largest amount of sample, the lowest sensitivity and selectivity, giving rise to high penalty points in figures of merit. Conversely, the advantage of this method is the low cost of determination.

The overall qualification of the different variables in the hexagon pictogram is assigned according to the penalty points assessed. For the sake of clarity, Fig. 2S shows the penalty points of each variable considered in the hexagon tool. Figures of merit are divided into two different groups, that is, one takes into account the sample treatment, method characteristics and calibration while the second one involves quality control and accuracy. Then, both groups are included in the variables of the method with the penalty points assigned to toxicity, safety and residues. Finally, the carbon footprint (Pla-Tolós et al., 2016) and annual cost (Ballester-Caudet et al., 2019) are computed numerically for each analytical method studied.

The proposed method for the ammonium determination was designed for being used in an environmental laboratory. For field work, for example a rapid monitoring of rainwater events, portable syringe filters and a smartphone with a free image RGB analysis software (Prieto- Blanco et al., 2019) could be of use.

The optimization for a possible industrial production could focus on the design of the analysis test. The commercial kit has to contain the hypochlorite/sodium hydroxide solution dosis, the properly packaged pieces of disc and a vial to carry out the reaction.

4. Conclusions

Aportable device based on the colorimetric Berthelot reaction was proposed for the analysis of rainwater. Images taken with an optic microscope supported the fact that the reagents (thymol, salicylate and nitroprusside) were embedded into PDMS. The figures of merit obtained showed that the PDMS sensor provided a suitable determination of ammonium using a low amount of rain-sample, which contributes to about a better understanding of rainwater and its ecological health. The application of the PDMS-SL-NP method to rainwater samples allowed studying the rainout and washout processes. For short events and fractionated samplings, a higher contribution of rainout process was found in the removal of ammonium ion from the atmosphere. In longer duration events, a relationship between the ammonium concentration and the sampling time could indicate the loss of ammonium over time. The environmental impact, the amount sample, sensitivity or selectivity were factors that distinguish the device among the different available methods. In this comparative study, the salicylate sensor has advantages mainly related to sustainability and sensitivity.

Declaration of competing interest

The authors declare no conflict of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.114911.

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