Electrochemical sensors for environmental gas analysis

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Abstract

The application of electrochemical sensors for measurement of concentration of pollutant gases in air in the part-per-billion (10^9) range is reviewed. Performance-limiting factors, particularly the effects of extremes and of relatively rapid changes in ambient temperature and humidity are noted. Variations in composition of the electrolyte in the meniscus at the electrode-gas interface, and instability of the solid-liquid-gas contact line, causing important variations in current due to background electrode reactions, are deduced and suggested as the reason for the performance limitations. Suggestions are made for mitigation through instrument design.

1. Introduction

Electrochemical sensors for environmental gas analysis have been in commercial practise and widely used for many years, for industrial health and safety monitoring [1]. In this application, measurement is at concentrations that approach a short-term hazard to human health (exposure times in the range of tens of minutes to 8 hr.): the scale is parts-per-million ($1:10^6$) by volume (ppm). The devices have proven to be reliable and robust. They use very little power and the response is linear, accurate and stable. In recent years, the same devices have come to be explored and then marketed for measurement of critical pollutant gases at concentrations found in the open atmosphere, typically in urban environments. These concentrations are on the scale of parts-per-billion ($1:10^9$) by volume (ppb): a factor of 1000 lower than the health and safety scale for which they were originally designed. With mounting concern over the long-term health effects of exposure to low concentrations of NO_2 and O_3, they are now being widely applied in low-cost sensor networks for measurement of these gases at ppb levels in urban atmospheres [2]. These low-cost sensor networks are being extensively investigated as a basis for community action [3] and their use, which raises interesting social science questions[4], is predicated on assumptions about the reliability of the resultant data [5, 6]. After a short summary of the extensive previous literature on electrochemical gas sensors, the present review focusses on the issues of measurement in the open atmosphere of ppb-scale concentrations with such sensors and highlights some little-appreciated and little researched aspects of the design and response characteristics. The reasons for subtle but important errors are suggested. Specifically, the role of meniscus electrochemistry is explored.

2. Key aspects of device construction

The key breakthrough in the development of electrochemical gas sensors was the use of a Teflon-bonded gas diffusion electrode [7], of a type originally developed for fuel cells. This electrode features a very large 3-phase (gas-electrode-electrolyte) interface area per unit volume. Important for sensor design is to provide a separate gas diffusion barrier, either as an orifice or as a porous membrane, such that the electrochemical reaction current is limited by diffusion in the gas phase through this barrier [1]. Diffusion within the electrode itself is not then a limiting factor, and the variability of electrode utilisation with gas concentration is not a factor affecting the analytical response. Other important design elements are the use of a quasi-reference electrode, which might also be the counter electrode, and construction such as to minimise the effect of ohmic resistance in

the electrolyte and to have an adequate reservoir of electrolyte to counter evaporation losses. Hence, devices are constructed in the form of a set of planar electrodes separated by thin porous support membranes that absorb electrolyte, with various configurations of wick to connect to a sealed electrolyte reservoir upon which the electrode assembly is mounted [8-10]. These aspects of design have been well-reviewed by Hobbs et al.[1], and repeatedly rehearsed in a number of reviews since. These reviews [11-14] have detailed developments particularly in electrolytes and applications, particularly for analytical devices at the ppm level. Problems of noise and background drift were mentioned early and the comment made that these phenomena were poorly understood [14]; those authors also noted that "the design and materials chosen for each part of the sensor are critical and determined, to a large part, by the application and the desired analytical performance". They further noted that "sensors based on metallized porous membranes and porous catalytic electrodes have been produced from several manufacturers that are widely used in industrial applications. On the other hand, relatively few publications on this specific structure of electrode have appeared in the scientific literature in the past decade, indicating the maturity of this type of device". One reason for a lack of publications on specific electrode structures is that obtaining a reliable and repeatable fabrication is generally more to do with art than with design. The importance of electrode microstructure was realised early in the development of this type of sensor [15]. The electrolyte penetration can vary a great deal depending on small variations in preparation [16]. Controlling such variation is a matter for systematic exploration and careful process control and hence is not disclosed by manufacturers. Recent academic literature has discussed methods for preparing electrodes with high sensitivity by exploring different types of nanoporous support, and methods for measurement of gases that are not electroactive. Recent reports on different supports directed towards measurements of different gases include composites of PTFE/Pt/multiwall carbon nanotubes (H_2) [17], carbon/Co_2P/Pd (formaldehyde)[18], Ir-decorated hollow graphene (NH_3)[19], Co_3O_4/reduced graphene oxide/carbon nanotubes (NO_2)[20]. Electrodes formed by pyrolysis of metal-organic-framework (MOF) structures to give metals, metal phosphides or metal carbides supported on high-porosity N- or P-doped graphitised material are being explored [21]. MOF-based electrode materials are being explored for sensing volatile organic compounds [22-24].

As is discussed later, whilst devices for a wide range of electroactive gases may be commercially mature and are used with confidence in the ppm concentration range, for the particular application of measurement at ppb concentrations in the open atmosphere, despite the promise and compelling early results, there are significant open questions and unsolved problems. On the other hand, for measurement problems that are better-controlled, commercial devices can give excellent results at ppb concentration. A particular example is the use for measurement of NO in exhaled breath [25, 26], an important clinical indicator for asthma. Another is the measurement of nitrite in food [27].

3. Measurement in the urban atmosphere

The possibility of using a simple amperometric gas sensor for measurement of NO and NO_2 at concentrations in the ppb range was noted some time ago [28]. The working electrode was Au sputtered onto PTFE. However, in that work electrochemical noise, and variations in background current probably dependent on the details of construction of the Pt-air quasi-reference electrode (QRE) used, were significant limitations. The use of Au and Pt deposited on Nafion for measurement of ppb-level concentrations was also reported [29] ; the key was the use of a concentrated sulfuric acid electrolyte to minimise interferences. Carbon as an electrocatalyst for NO_2 measurement has been explored [30], and used commercially [10]. Recent reports have claimed ppb-level sensitivity for NO_2 in air [31] using ionic liquid electrolyte [32-34] . The use of ionic liquid electrolytes in gas sensors has recently been reviewed [12].

The use of commercial electrochemical sensors for measurement in the urban atmosphere, and the deployment of a low-cost network using these sensors was introduced by Mead et al. [35]. There has been subsequently an explosion of reports using commercial electrochemical sensors in low-cost networks, with rather mixed results: for example [3, 6, 36-40]. Progress in this application area was recently reviewed by Baron and Saffell [2]. Networks of electrochemical sensors, employing data correction methods that use independent information for validation [5], have been applied very effectively to resolve neighbourhood-scale variations of NO_2 concentration and to identify sources of significant local pollution [39-42]. The advantage of using commercial devices, well-established as health and safety monitoring tools, is that they are robust, reliable and repeatable. The disadvantage is that the details of construction and composition of the electrodes and the composition of the electrolyte is proprietary, so understanding the origin of subtleties in behaviour that impact on performance becomes difficult. Selectivity of response is an important issue. Some selectivity may be achieved by choice of electrode material and electrolyte as well as by adjustment of electrode potential. The literature is not very detailed. Table 1 sets out reports relevant to the measurement of NO and NO_2 in the atmosphere. Ozone constitutes a significant interference in the measurement of NO_2. The interference may be handled by the use of a catalyst applied over the sensing electrode to decompose ozone [43], and by the use of an independent ozone measurement to correct the measured current for the interference : a semiconducting oxide-based sensor for ozone has been used very effectively for that purpose [39, 40].

Table 1 Aqueous electrochemical cells for measurement of NO_2 and NO in air

ref	gas	electrolyte	electrode	Reference electrode	E / V (wrt ref electrode)	comment
[28]	NO_2	30 wt% H_2SO_4	Au sputtered on PTFE	Pt-air QRE	-0.2	ppb concentrations. Background current sensitively dependent on cell configuration. QRE potential given as 1.00 ± 0.03 V RHE [44].
	NO				+0.4	
[45]	NO_2	4 M H_2SO_4	Au/PTFE composite	Hg/Hg$_2$SO$_4$	+0.6 - +1.0 (RHE)	Clear diffusion-limited current. NO, NO_2, CO specificity obtained by choice of electrode material. CO: Teflon-bonded Pt; NO, NO_2: Teflon-bonded Au; CO oxidation rises with onset of Au oxidation at 1.0V then drops abruptly at 1.4V With Pt / PTFE composite electrodes, the background current was similar to the signal current for ppm-scale concentrations [46]
	NO				+1.0 - +1.5 V RHE	
[30]	NO_2	2.5 – 5M H_2SO_4	Edge-plane graphite	Graphite QRE	-0.2	Reversible electrode in 5 M H_2SO_4 No observable reduction reaction at acid concentration < 2.5 M on this electrode. Specific effect of edge-plane graphite.
[10]	NO_2	H_2SO_4	Various carbon inks supported on PTFE			Results strongly dependent on source of the carbon. Different carbons differ significantly in hydrophilicity leading to important variations in electrolyte filling of a composite with PTFE and of current distribution around the meniscus [16, 47]
[48]	NO_2	5 M H_2SO_4	carbon nanotube			Miniaturised printed sensor featuring polymer layers laminated together,
[49]	NO_2	0.5M H_2SO_4	Pt / Nafion	Ag/AgCl	+0.8	Time-varying changes in Pt oxide reduction current limited observation of NO_2 reduction current

[50]	NO₂	0.5M H₂SO₄	Au / Nafion	Hg/Hg₂SO₄	+0.85 (RHE)	Need for background current subtraction. Results also presented for O₃ and SO₂
	NO				+1.15 (RHE)	

4. Important performance-limiting issues

Sensitivity of standard electrochemical devices to concentrations of interest in the urban atmosphere is not a problem [39]. Effects that are important in the application to measurement in the urban atmosphere were noted in the original report by Mead et al. [35]: cross-sensitivity between NO_2 and O_3 [50]; a significant temperature dependence of the measurement baseline; a significant electrochemical noise on measurement in the atmosphere which was not present in laboratory measurement; and an effect of wind speed. Machine-learning methods for calibration have been applied with mixed success and extensively discussed: for example [3, 51-54]. These methods require auxiliary measurements of temperature and relative humidity, and at least one other sensor that has a different pattern of cross-sensitivity. A major issue is that, if the range of the variables that influence the result moves out of the range under which the response model was developed, then the model becomes unreliable [54-56] – an effect that is termed 'concept drift' [56]. Furthermore, in a commercial instrument the model applied to derive the result from the observations is often hidden. If the assumptions either explicitly or implicitly made in going from an observation or measurement to a reported result are hidden, inappropriate, difficult to determine, or unacceptable then the believability of the result will be low [5]. Data fusion with additional, independent information , and the use of a hierarchical network, where statistical comparisons between the results from a widespread network of low-cost devices and a sparse network of high-quality regulatory-grade instruments are used to correct the results from the low-cost instruments, has proven successful in delivering reliable data [5, 39, 40]. However, the effects of large local temperature and humidity variations remain difficult to account for in a reliable and simple way and remain an obstacle to progress [40].

Mead et al. [35] supposed that the electrochemical noise observed for measurement in the atmosphere was a real effect reflecting very large and rapid fluctuations in atmosphere composition. The electrochemical noise was noted particularly also by Weissert et al. [39], who speculated on meniscus fluctuations rather than atmosphere composition fluctuations as the cause. The noise was so large with respect to the signal that signal averaging over a significant time (at least 15 min up to 1 hr) was needed to extract the time-varying atmospheric concentration. In laboratory measurements, the noise was absent and measurement to low ppb concentrations could easily be made.

The effects of variation of temperature and atmospheric humidity are subtle and important. There is a significant variation of baseline with ambient temperature, equivalent to an activation energy of ~ 70 kJ mole^{-1} [35]. Simple methods can be derived to correct for this if the ambient temperature does not change too suddenly or become too extreme [35, 54, 57]. More subtle and important are effects of extremes and of sudden changes, which occur more or less frequently depending on the region of the world. A step change in humidity causes a step change in current, which then leads to a slow relaxation of the background current [58, 59]. Similarly, extremes of temperature, and rapid temperature changes, lead to a significant shift of current and to a slowly relaxing, persistent effect on the baseline current [40] : Figure 1. Because of these effects, laboratory calibrations cannot reliably be applied for field use, and, as noted above, machine-learning approaches for field

calibration give unreliable results when the range of parameters, such as temperature and rate of change of temperature and humidity, move outside the range for which the model has been constructed.
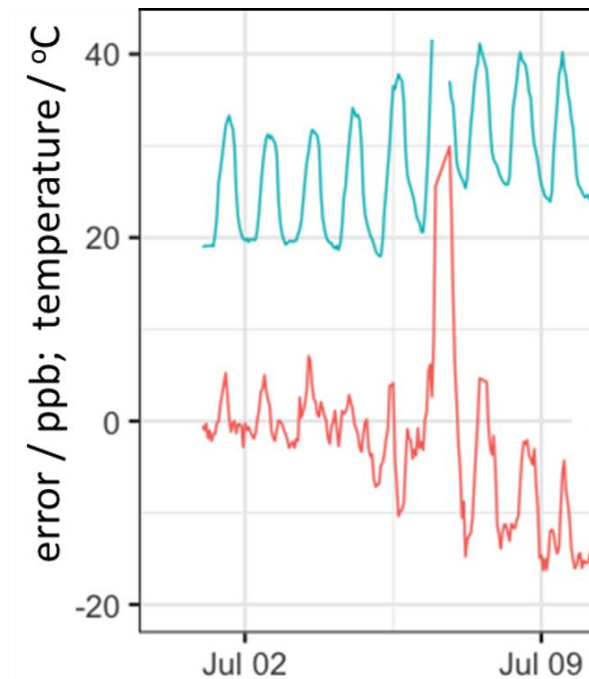

Figure 1 Persistent error in NO_2 concentration indicated by an electrochemical sensor as a consequence of ambient temperature excursion to an extreme value. Red: error (difference between sensor-indicated concentration and actual concentration; green: ambient temperature. From results reported by Weissert et al. from a sensor network installed in Southern California [40]; © Elsevier, reproduced with permission.

5. Discussion of meniscus electrochemistry as the origin of performance-limiting effects

The origin of these performance-limiting effects is currently unknown. However, it seems that the key is variation in the rate of background electrode reactions, and reasonable speculations can be made on the basis of known effects at the electrode-electrolyte-gas meniscus. These, discussed below, are: variations with humidity of equilibrium electrolyte composition in the meniscus and consequent variations of interfacial tension; fluctuations in QRE potential caused by temperature changes or by electrolyte composition changes resulting from proximity to the sensing electrode, leading to changes in sensing electrode potential and hence changes in interfacial tension; and effects of meniscus motion. The electrode structure leads to multiple mechanically metastable states of the solid-liquid-gas contact line; normally the contact line would be pinned in a particular state, but pressure fluctuations or equilibrium liquid composition changes could lead to transitions between different configurations of the contact line. Effects of convection due to temperature and interfacial tension gradients associated with exchange of water with the atmosphere could add further complication.

Teflon-bonded gas-diffusion electrodes have been extensively studied since they are a critical fuel cell component. Giner and Hunter [60] developed the description of these as two inter-penetrating

continuous networks, each comprising porous agglomerates: one of these networks comprises the hydrophobic phase through the porosity of which the gas diffuses, and the other network comprises the hydrophilic electrode material, whose porosity is flooded with electrolyte. The mathematical description of this system was developed by representing the electrode phase as a porous cylinder contacting gas uniformly around its surface. The electrode reaction occurred throughout the cylinder, with gas diffusing from the cylinder face. In the gas sensor application, the assumption is that the reaction rate for the analyte is sufficiently fast that the current is limited by diffusion to the external surface of the electrode and thus not sensitive to details of the current distribution or reaction rate within the electrode. However, this is not necessarily the case for the background current, which is likely to be dominated either by oxygen reduction or electrode oxidation, depending on the electrode potential. The background will be sensitive to the actual electrode area in contact with electrolyte and to the actual electrolyte composition within the electrode structure. An electrode structure comprising a double interpenetrating network permeated in one phase by gas and in the other by electrolyte implies an interface between gas, solid and electrolyte that has a complex shape [61]: a fractal meniscus rather than a simple, smooth interface. It is reasonable then to assume that the meniscus, and any thin liquid film that is attached to the meniscus and wetting the active, hydrophilic electrode network, will be in equilibrium with water vapour in the gas phase. The consequences for the composition of a sulfuric acid electrolyte are easily calculated: Figure 2.
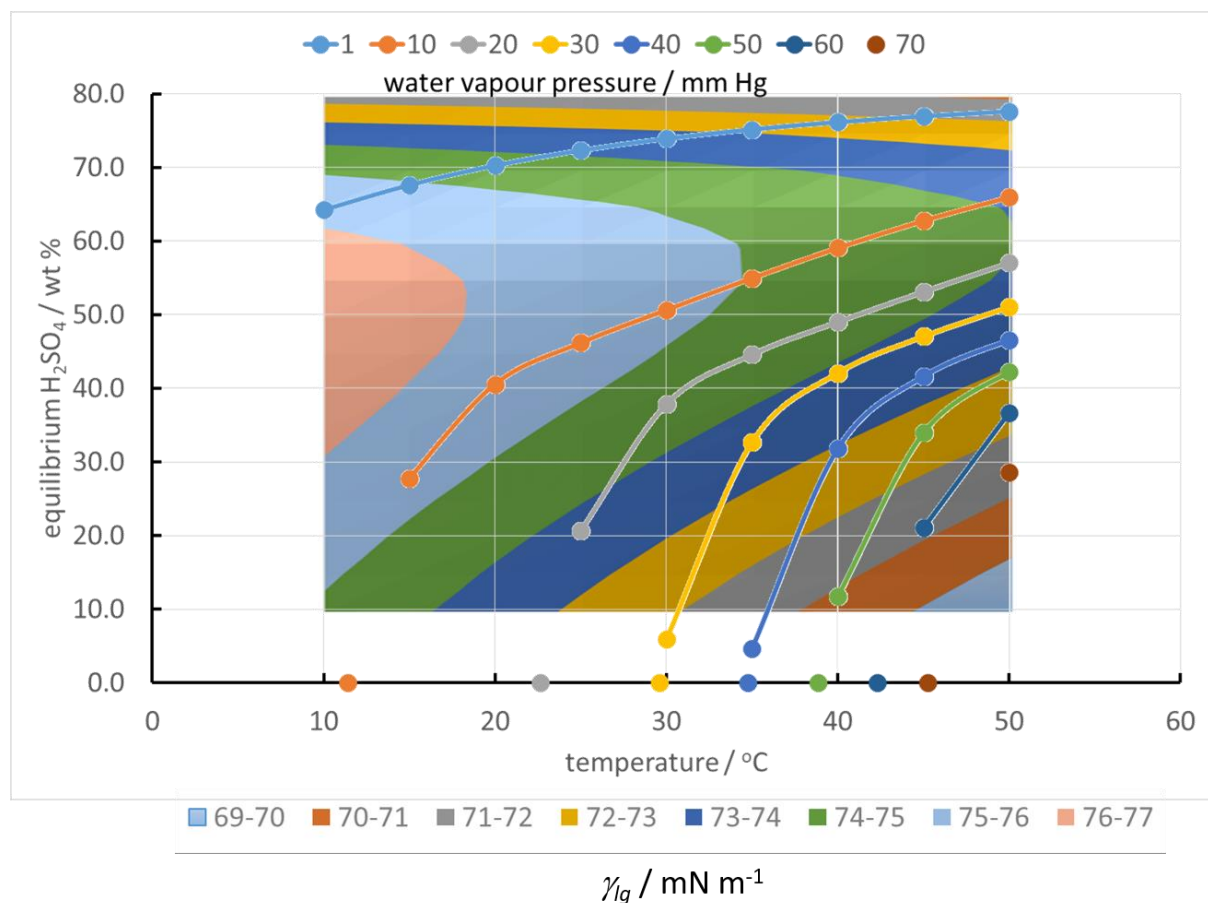

γ_{lg} / mN m^{-1}

Figure 2. Concentration and interfacial tension, γ_{lg} of aqueous H_2SO_4 in equilibrium with water vapour at varying temperature. Lines: concentration vs temperature for various fixed water vapour

pressure. Background shading: γ_{lg} as a function of concentration and temperature. Data sources are [62, 63]

As shown in Figure 2, there are ranges of temperature and water vapour pressure where the equilibrium composition of the electrolyte would vary very strongly if either temperature or water vapour pressure changed. For example, a change from 30°C to 45°C as in Figure 1, with a water vapour pressure of 30 mm Hg would cause a change in equilibrium composition from 5 to 45 wt % H_2SO_4 . Similarly, interfacial tension can vary by as much as 10%. Depending on the electrode reaction and electrode material, the changes in electrolyte composition in the meniscus could have a significant effect on the background electrode reaction rate, with a resulting effect on the measured current dependent on the fraction of the total current accounted for by the meniscus within the porous electrode structure. In particular, at the electrode potential for reduction of NO_2, oxygen reduction is likely to constitute the background current. The rate of this reaction in strong sulfuric acid is strongly dependent on acid concentration [64]. Furthermore, even at low overpotential a significant current for oxygen reduction would come from a part of the electrode surface close to or above the upper edge of the meniscus, the current distribution being determined by the meniscus shape, hence by the interfacial tension, and by the electrolyte conductivity in the meniscus [64-66]. Associated with the changes in composition of H_2SO_4 would be changes in enthalpy generation within the meniscus, leading to a temperature gradient within the electrode and particularly just behind the meniscus. Gradients of temperature and interfacial tension can give rise to convective motion of the liquid and instability of the solid-liquid-gas contact line: another phenomenon that has been much studied [67-69]. The important point is that, when the reaction current due to the analyte is small, then even small variations in background current can become significant.

Now, the question arises: what exactly is the shape of the electrocatalyst-electrolyte-gas contact surface, and is this indeed of any importance? For a slab thickness, h, of uniform spheres, radius r_0, wetted by a liquid with contact angle θ, where $\theta < 90°$, the liquid will fill the slab to the outer surface, such that at every point where solid, liquid and gas are in contact, the contact angle is θ. For an array of spheres on a regular lattice terminating in a single plane, there is a unique solution for the solid-liquid-gas contact line: on the terminating plane, the surface will display a regular array of caps of spheres, each of radius $r_c = r_0\cos\theta$ and the liquid-gas interface will be defined by two radii of curvature which will be everywhere the same. However, if the liquid has to contact an irregular surface, within the pores of an interpenetrating network of two solids each comprising irregular particles, with the constraint simply that the contact angle at all points where the liquid meets one phase should be θ, then the radius of curvature of the liquid-gas interface could with some probability adopt any value within a distribution ranging from zero to $h / 2\cos\theta$. Hence, the solid-liquid-gas contact line will have multiple possible stable configurations and hence be mechanically metastable, able in principle to switch between any of these configurations at random, in response to some small perturbation. The distribution of possible radii of curvature of the contact line will be affected by the size and shape distribution, and the volume fraction of both types of particle comprising the electrode structure. "Pinning" of the solid-liquid-gas contact line – resistance to movement of the contact line in response to a mechanical perturbation or change in temperature – has been much studied [70-72]. Surface roughness and chemical heterogeneity are important parameters and the dynamics are strongly affected by the composition and properties of a very thin wetting film over the solid surface in advance of the meniscus [71, 72]. A mechanical perturbation could be a change of pressure applied across the interface, or a change of interfacial tension. It has been noted above that significant changes of interfacial tension can arise as a result of changes in

electrolyte composition caused by changes in temperature or humidity. Therefore, it is reasonable to suggest that the instabilities in background current caused by changes in temperature or humidity could be due to movement of the solid-liquid-gas contact line. These movements could be small, between configurations that are locally similar, or large, between configurations that are locally very different, depending on the magnitude of the perturbation.

Fluctuations in the contact line causing fluctuations in the background current could also be an explanation for the electrochemical noise, in which case this is indeed an artefact rather than reflecting any subtlety of atmospheric chemistry or mixing. The fluctuations could arise because of exchange of water and its transport between the meniscus region and electrolyte leading to temperature, composition and interfacial tension gradients which could result, as noted above, in contact line instability dependent on details of the electrode construction. However, it is also assumed that the external pressure is the same on both faces of the electrode. This is not necessarily true: one face is enclosed and the opposite one is exposed to a chamber which is connected to the atmosphere through an orifice. Two effects might then cause pressure fluctuations of relatively high frequency which could cause movement of those sections of the contact line where the Laplace pressure associated with the radius of curvature was smaller than or similar to the pressure difference between the front and back of the electrode. The first is acoustic noise. The second is an acoustic resonance ("Helmholtz resonance") caused by the passage of the wind across the external orifice of the sensor, exciting the resonance within the chamber above the sensing electrode. Weissert et al. [39] noted that the electrochemical noise could be significantly diminished by mounting the sensor at the base of an open tube. In their work, the noise was not correlated with the average signal (ie not correlated with the indicated NO_2 concentration) but there was a clear effect of the time of day – high noise was more likely in the middle of the day, when the acoustic noise on a busy commercial street would be greatest. An effect of wind has been noted by Mead et al. [35], and their results also showed the noise to be largest in the middle of the day.

6. Conclusion

Electrochemical sensors can certainly measure accurately the concentration of various pollutant gases in air, when they are operated under controlled conditions. Use of the sensors directly in the atmosphere has led to a number of issues that are difficult to resolve, which in general have nothing to do with the basic principle of operation of the sensor but which instead reflect on the overall design of the instrument using the sensor and the measurement system within which it is deployed. There is a design conflict between two points of view. The first is "low cost at all costs", and assumes that computational manipulation of the data will overcome the limitations. That approach raises questions about the believability of the results [5]. The second view is to pay attention to detail in aspects of instrument design and gas sampling, particularly temperature control, a pumped-flow air sampling system and buffering humidity changes using Nafion® inlet tubing [73]. This approach would certainly increases the cost of the instrument but would equally certainly pay dividends in the quality and reliability of the resulting data.

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