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CRITICAL REVIEW OF INNOVATIVE AND CLASSICAL METHODS FOR ANALYZING NITROGEN OXIDES IN AMBIENT AIR

Venera-Stanca NICOLICI, Ahmed ADJAL, Ioana IONEL

Abstract: *This study presents a comparative critical analysis of reference and alternative standard methods for ambient nitrogen oxides (NO_x) measurement. It systematically evaluates established techniques, such as chemiluminescence, alongside emerging alternatives including spectroscopic sensors and passive sampling devices. The paper highlights the strengths and limitations of each method, focusing on their metrological performance, cost-effectiveness, and operational practicality within large-scale monitoring networks. Findings reveal a key trade-off between the uncompromising accuracy of reference methods and the broader feasibility of alternative approaches. Ultimately, this analysis provides a framework for selecting the most suitable methodology based on monitoring objectives, resource availability, and required data quality.*

Keywords: *Nitrogen Oxides (NO_x); Air Quality Monitoring; Reference Method; Equivalent Method; Low-Cost Sensors; Electrochemical Sensors; Passive Sampling; Environmental Innovation*

1. PROBLEM DESCRIPTION

Regulatory control of nitrogen oxides (NO_x) is universally mandated, to comply with EU directives, WHO (World Health Organization) standards and implement effective air quality policies. Air pollution emissions have declined in the last two decades, resulting in better air quality. Between 2005 and 2022. Despite this improvement, air pollution remains the largest environmental health risk in Europe. Exposure to nitrogen dioxide cause an estimated 48,000 premature deaths in 2022. The WHO's 2021 updated global air quality guidelines set an annual mean limit for NO_2 of 10 µg/m³ (~5 ppb) in the USA, a drastic reduction from the previous 40 µg/m³ (which remains the upper limit in Europe), reflecting the growing evidence of its toxicity [1].

Nitrogen Oxides (NO_x) are primarily generated through high-temperature combustion processes, where atmospheric nitrogen (N_2) and oxygen (O_2) react. Key sources include:

- Transportation, which is the dominant source in most urban areas. Diesel vehicles involved in road traffic emit significantly higher levels of NO_x per kilometer, compared to gasoline. The 2015 "Diesel gate" [2] scandal highlighted the discrepancy between regulatory tests and real-world emissions. Non-road vehicles, such as shipping, aviation, and rail transport are major, often under-regulated contributors. International shipping alone accounts for an estimated 10% of global NO_x emissions from transportation [3].
- Energy production and industrial combustion (stationary sources) include power plants, industrial boilers and furnaces, residential and commercial heating. In the US, EPA (The Environmental Protection Agency) reported for 2024 that 49% of total NO_x emissions are coming from these sources [4].
- Other sources, such as agriculture, natural sources (such as lightning and wildfires), with small contribution compared to anthropogenic sources.

According to the European Environment Agency (EEA), 49.83% of total NO_x emissions in the EU in 2023 came from the transport sector, followed by agriculture (13.77%), the energy industry and manufacturing, and extractive industry, each one with a contribution of 12.81%

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and last, residential and commercial heating with 9.71% [5].

Effective NO_x management and regulatory compliance are guided by standards set by governing organizations like the European Committee for Standardization (CEN), the International Organization for Standardization (ISO), and the US EPA. These are fundamentally dependent on the accuracy and reliability of analytical data. However, air quality monitoring agencies and researchers face a critical dilemma in selecting an appropriate methodology. This dilemma comes from a pronounced compromise between the superior metrological performance of Reference Standard Methods (SRM), such as chemiluminescence, and the operational and economic feasibility of emerging alternative techniques.

Reference methods provide legally defensible data but are costly and impractical for dense deployment. Alternative methods like spectroscopic sensors or passive samplers offer cost-effective scalability but can sacrifice data quality, such as precision, accuracy, or temporal resolution. This creates a core challenge: balancing uncompromising compliance-grade data with the practical need for widespread coverage.

Therefore, there is a pressing need for a clear, critical framework to guide the selection process. The scope of this study is to identify and describe SRMs for NO_x and related standards, in correlation with the alternative methods. Moreover, to perform a critical comparative analysis based on technical, economic and operational parameters, but also to propose future directions for research and development. Although many studies focus on individual methods, few provide a comprehensive, criteria-based comparison across categories.

This study reviews NO_x measurement methods for policymakers and air quality specialists. It compares standardized, equivalent, and alternative techniques, establishing evaluation criteria and highlighting the key advantages and disadvantages of each approach.

2. METHODOLOGICAL FRAMEWORK FOR CRITICAL ANALYSIS

2.1 Description of analysis methods

This study identifies all regulatory and technical documents for NO_x analysis in ambient air and emissions. The methods were classified by regulatory recognition into three categories: Standard Reference Methods (SRM), Equivalent Methods (EQM), and Non-Standardized Methods (NSM). Standardized methods were sourced from official European, American, and Romanian bodies, while non-standardized techniques were reviewed through specialized literature and articles available on online platforms [6-25].

Are legally defined analytical procedures for measuring air pollutants, serving as the official benchmark for regulatory compliance. In Europe, the current SRM is based on the chemiluminescence principle, which replaced older, now-obsolete standardized techniques. The USA employs similar SRMs, primarily using chemiluminescence or other approved principles. Table 1 lists the specific European and American SRM standards for NO_x measurement.

Table 1

SRMs in Europe and the USA.

Standard	Method	Technology Principle
Ambient Air		
SR EN 14211: 2025	CL	CL
ISO 7996:1985 - obsolete		
ISO 6768: 1998 - obsolete	Modified Griess-Saltzman method	Colorimetry
Stationary source emissions		
EN 14792: 2017	CL + UV Spectrophotometry (as EQM)	CL
EPA Method 7E (US)	CL	CL
EPA Method 7B (US)	UV Spectrophotometry	UV Absorption
EPA Method 7C	Alkaline-Permanganate/ Colorimetric	Chemical Absorption/ Colorimetric
EPA Method 7D	Alkaline-Permanganate/Ion Chromatographic	Chemical Absorption/ IC
EPA Method 7A (US) referee method for calibration	Ion Chromatography (IC)	Chromatography

Standard	Method	Technology Principle
ISO 11564: 1998 - obsolete	NEDA photometric method	Colorimetry+ photometry
EPA Method 7 (US)-obsolete	Phenoldisulfonic Acid (PDS)	Colorimetric

The main standardized method is based on chemiluminescence, which is the emission of light during a chemical reaction. The process of measuring NO and NO_2 based on chemiluminescent reaction begins with the gas-phase reaction between nitric oxide and ozone:

$$NO + O_3 \rightarrow NO_2^* + O_2 \quad (1)$$

Where:

NO_2^* is the excited molecule of NO [11].

The reaction releases significant energy, exciting the newly formed NO_2 molecules to a higher, unstable energy state. As they rapidly return to ground state, they emit the excess energy as photons of light.

$$NO_2^* \rightarrow NO_2 + hv \quad (2)$$

Where:

h is Planck's constant

v is the frequency of the light [11].

The intensity of emitted light, which is directly proportional to the NO concentration, is measured to quantify NO. To measure total NO_x, a parallel sample stream is first directed through a converter that reduces NO_2 to NO.

$$NO_2 + (heat\ or\ light) \rightarrow NO + O \quad (3)$$

[11]

This converted gas stream, which now contains the original NO plus the NO that came from NO_2, is sent to the reaction chamber. The measured value is called "NO_x" ($NO + NO_2$).

Other standardized methods are based on the colorimetry principle, such as the modified Griess-Saltzman method and the naphthyl ethylenediamine photometric (NEDA) method. Both are manual laboratory methods that involve a wet chemical technique, with air or flue gases emitted from stationary sources, such as industrial stacks, boilers, and furnaces, being actively extracted through a solution and then analyzed.

In Griess-Saltzman method, NO_2 is absorbed and converted into a stable nitrite ion [27] in solution and then converted to a pink azo dye. The concentration of NO_2 is determined by measuring the intensity of the resulting pink color with a spectrophotometer, as the color density is directly proportional to the NO_2 level. While obsolete as a reference method since the adoption of chemiluminescence, its chemistry remains fundamental in passive samplers. Similarly, the NEDA method, though replaced, still serves as a reference for calibrating continuous emission monitoring systems (CEMS).

Along with chemiluminescence, the following SRMs are active in the USA:

- The Phenoldisulfonic Acid (PDS) Method is a classic laboratory technique where NO_2 is collected and converted to nitrate, which then reacts with PDS to create a yellow compound. The intensity of this color, measured spectrophotometrically, determines the nitrate concentration.
- UV Spectrophotometry Method is an instrumental method for continuous measurement. It directly measures NO_2 by detecting the amount of UV light absorbed in a sample cell. It does not measure NO directly.
- Alkaline-Permanganate/Colorimetric is a wet-chemical technique that oxidizes NO_2 to nitrate in an alkaline solution, then uses a color-forming reaction to measure the concentration based on the intensity of the resulting color.
- Alkaline-Permanganate/Ion Chromatographic is a two-step technique where NO_2 is first oxidized to nitrate in an alkaline permanganate solution, followed by precise quantification of the nitrate ions using ion chromatography.

So, the chemiluminescence method is established as a Standard Reference Method (SRM) for measuring NO_x in both ambient air and stationary source emissions. In the US, standardized colorimetric, spectrophotometric, and ion chromatographic methods are also recognized for compliance monitoring.

After analyzing the reference methods, we now focus on **equivalent methods (EQM)**, which are alternative, non-reference techniques, widely used for measuring NO_x. These methods are often used for continuous monitoring, research, or screening purposes, but don't respond to compliance requirements.

Table 2 presents the list of standards and technical specifications identified in Europe and in the USA as Standardized Equivalent Methods (EQM) for measuring NO_x.

The rapid growth of air quality sensors necessitates their inclusion in formal standards. In response, European (CEN/TS 17660-1) and American (ASTM - Advancing Standards Transforming Markets) bodies have established testing protocols to validate sensor performance against reference methods. These standards provide a "fit-for-purpose" framework, building a chain of trust for a new, scalable monitoring infrastructure. While SRMs remain the definitive benchmark, these new guidelines unlock the practical potential of sensor technologies.

The ISO 10849 standard ensures Automated Measuring Systems (AMS/CEMS) produce reliable, compliant data for monitoring emissions.

Table 2

EQMs in Europe and the USA.

Standard	Method	Principle
Ambient air		
CEN/TS 17660-1:2021, ASTM D8406-22 + ASTM D8559-24 (USA)	Electrochemical (EC) and Optical Sensors, Metal Oxide Semiconductor (MOS)	Test against SRM
EN 16253:2013	Active DOAS (Differential optical absorption spectroscopy)	DOAS
EN 16339:2013	Diffusive sampling	Colorimetry or IC
Stationary source emissions		
ISO 10849: 2022	Performance characteristics of AMS	CL, Spectroscopy (FTIR), Infrared absorption (NDIR), UV absorption (NDUV)
ASTM D6348-12:2020 (Test Method)	Portable FTIR	Infrared absorption
Equivalent with EN 14792	Using EN 14181:2014 and EN 14793:2017	Photolytic converter using UV light
EN 14793:2017	Equivalence of an alternative method with a reference method	Statistical

This performance-based framework sets strict validation thresholds for all major NO_x measurement techniques, creating the critical link between advanced instrumentation and environmental regulation. These techniques include chemiluminescence (CL), non-dispersive infrared (NDIR), which measures absorption of infrared light by NO, Fourier Transform Infrared (FTIR), which uses infrared spectroscopy, and other techniques, such as ultraviolet (UV) spectroscopy.

While ISO 10849 is the continuous surveillance standard and it is about long-term, automated performance, another standard is related with short-term, investigative precision for multiple parameters, like a "detailed diagnostic" standard (ASTM D6348-12). A facility that uses CEMS certified to ISO 10849 for its continuous NO_x compliance reporting, could perform periodically a test using ASTM D6348-12 with an FTIR to validate the CEMS's performance, measure other unmonitored pollutants, or characterize emissions during a specific process upset.

DOAS (Differential Optical Absorption Spectroscopy) is the primary method for monitoring ambient air over long, open paths and is standardized in EN 16253. This technique is ideally suited for measuring air quality across areas like street canyons, urban spaces, and industrial fence lines. A key application is the quantification of diffuse (fugitive) emissions from large sources, including landfills, wastewater treatment plants, and vast industrial sites. The method enables the calculation of total emission fluxes, providing results in g/s or kg/h for specific gases. The method relies on the precise measurement of the attenuation of light by gaseous molecules across a known path length in the open atmosphere [28]. The technique detects pollutants by shining a UV/Vis (visible) light beam over an open path and analyzing the returned light. Each gas absorbs specific wavelengths like a fingerprint, and by using Beer-Lambert law [29], the software calculates the average concentration along the entire path length.

A common manual technique for determining the long-term average concentration of NO_2 (over 2-4 weeks) is passive diffusive sampling, standardized in EN 16339. Unlike automated methods that give hourly readings, this approach uses a sampler that collects NO_2 via molecular diffusion, requiring no power or pumps. The exposed sampler is later analyzed in a laboratory, where the absorbed NO_2 is chemically converted into a colored compound. The intensity of this color, measured by spectrophotometry or ion chromatography, is used to calculate the average concentration over the deployment period.

An alternative method for converting NO_2 to NO used in advanced chemiluminescence-based NO_x analyzers is the photolytic converter, which operates on the principle of photodissociation: a powerful UV light source acts like a molecular “chipper”, breaking apart the larger NO_2 molecules into smaller NO pieces within a reaction chamber. The system counts all the NO pieces, both the original ones and those created from NO_2, to report the total quantity of NO_x.

These alternative methods can also be equated with reference methods, using standard EN 14793, which provides the statistical framework and methodology for proving that an alternative measurement method (e.g., a new type of analyzer) gives results that are equivalent to those obtained by the SRM mandated for regulatory compliance. The process requires the alternative method (e.g., an analyzer with a photolytic converter) to be installed and operated in parallel with the regulatory SRM (e.g., the standard chemiluminescence method) for a defined period. Data from both systems is collected simultaneously and then statistically compared for accuracy and precision. The alternative method is certified as equivalent only if the results meet the standard's strict, pre-defined criteria. Therefore, air quality monitoring has moved beyond a single reference method, succeeded by a dynamic ecosystem where standards-validated alternatives provide the necessary flexibility, scalability, and complementary data.

The last category, **non-standardized methods (NSM)**, operates outside regulatory frameworks and doesn’t have formal validation. This category includes two distinct types of technologies:

- Advanced research instruments, with exceptional precision for scientific use. Examples include laser-induced fluorescence (LIF) – makes molecules fluoresce for detection; tunable diode laser absorption spectroscopy (TDLAS) - reads a gas's unique absorption "fingerprint"; cavity ring-down spectroscopy (CRDS) -measures gas concentration by how quickly light decays in a mirrored cavity; long-path absorption photometer (LOPAP) - traps gas in a liquid to create a measurable color change.
- Low-cost sensors, based on electrocatalytic principles. These are affordable, but have limitations like sensitivity to temperature, humidity, cross-interferences, and signal drift.

Their documentation status and scope are detailed in Table 3. In summary, NSMs fulfill non-regulatory roles, from providing data with research-grade techniques to enabling widespread spatial mapping with low-cost sensors and so expanding the scope and application of NO_x measurement.

Table 3

NSMs for NO_x.

Method	Status	Scope
Advanced Laser-Based Optical Techniques		
Cavity Attenuated Phase Shift (CAPS)	Research-grade; ISO 10849 + EN 14793 (it can be equated)	Air Quality/Emissions Monitoring, Scientific Research
Cavity Ring-Down Spectroscopy (CRDS)		High-sensitivity atmospheric research
Tunable Diode Laser Absorption Spectroscopy (TDLAS)		Highly specific, quantitative, and real-time data
Laser-Induced Fluorescence (LIF)	Gold-standard research technique	Combustion and atmospheric research
Advanced Wet-Chemical Techniques		

Method	Status	Scope
Long-Path Absorption Photometer (LOPAP) for NO_2	Research-grade measurements and validation of other methods	Research, validation, and low-level monitoring
Electrocatalytic reduction or oxidation		
Low-cost sensors	Workshop Agreement of CEN (CWA 17934:2021)	Screening, mapping, and public information

2.2 Criteria for evaluation

The starting point of comparative analysis is the need to explain the similarities and differences between objects; therefore, the universalizing comparative analysis and the differentiating comparative analysis coexist [30]. The evaluation of NO_x measurement methods is grounded in analytical chemistry, metrology, and environmental engineering. The goal is to establish a comprehensive framework that assesses each method’s performance against core scientific and regulatory requirements. Evaluation parameters are systematically defined to reflect the measurement process and context, balancing legal standards with practical operational feasibility.

Using multi-parameter comparison [31], the critical analysis highlighted the common and unique parameters of the analyzed methods. The selected parameters form a comprehensive framework to evaluate a method's performance against the fundamental equation of an analytical measurement [32]:

$$Reported\ Value\ =\ True\ Value\ +\ Systematic\ Error\ (Bias) +\ Random\ Error\ +\ Interference\ Effects \tag{4}$$

A multi-parameter matrix creates a structured, weighted framework to objectively evaluate and select the optimal method for a given application, considering specific needs, constraints, and regulatory demands. The evaluation criteria are organized into four fundamental scientific pillars, as detailed in Table 4.

Table 4

Multi-parameter evaluation matrix of methods.

Parameter	Significance
Analytical Performance	
Accuracy	Measures systematic error against primary standards
Precision	Measures random error
Selectivity/ Specificity	Resistance to interferences (e.g., PAN, O_3, H_2O, CO_2)
Detection Limit (LOD/LOQ)	Governed by S/N ratio
Applicability	
Suitability - Ambient Air	Assesses performance in low-concentration, multi-interferent environment requiring high sensitivity
Suitability - Stack Emissions	Assesses robustness to harsh conditions (high T, moisture, particulates) and high concentrations
Measurement Range	Expected concentrations (ppb for ambient air, ppm/ppmv for stack)
Operational Feasibility	
Time Resolution	Dictated by physics of detection
Portability	Spatial mapping, fence line monitoring, and mobile surveys
Initial Capital Cost	Cost of certified, hardware
Operational & Maintenance Cost	Cost of consumables, maintenance, and calibration
Regulatory Acceptance	
Ease of Use / Automation	Operator-induced error
Multi-Species Capability	Ability to measure co-pollutants (e.g., SO_2, NH_3, CO) simultaneously from same sample
Regulatory Acceptance	Certification that the entire measurement system controls uncertainty for legal compliance

Below are detailed parameters used to evaluate NO_x measurement methods.

2.2.1 Analytical performance characteristics

- **Accuracy** (Bias/Trueness): measures systematic error: the deviation of a measured value from the true value. For SRM and EQMs, accuracy is rigorously proven against traceable reference materials, ensuring metrological validity. NSMs must also demonstrate accuracy through strict validation protocols.
- **Precision:** Measures random error. High precision is necessary to differentiate true concentration changes from instrumental noise,

impacting detection limits and overall uncertainty.

- **Selectivity/specificity:** The method's capacity for exclusive target analyte detection, crucial for overcoming inherent interferences like converter non-specificity in chemiluminescence or spectral cross-sensitivity in optical analysis.
- **Detection limit:** Determines the lowest measurable concentration based on signal-to-noise ratio. This parameter is crucial for ambient air monitoring at ppb levels, but less critical for high-concentration stack emissions.

2.2.2 Applicability

- **Suitability:** Recognizes that methods optimized for one environment may fail in another. Stack monitoring requires robust systems for harsh conditions, while ambient monitoring demands high sensitivity and stability for low-level measurements.
- **Measurement range:** The analyzer's operational range must match expected concentrations, as stack and ambient environments differ by orders of magnitude.

2.2.3 Operational feasibility

- **Time resolution:** The measurement frequency is determined by the technique's physics, ranging from real-time (<60 seconds) for capturing peaks to integrated averages over weeks.
- **Portability:** Determines spatial coverage capability, from single-point stationary analyzers to mobile systems enabling pollution mapping.
- **Capital cost:** Initial investment varies from high, for certified analyzers (including rigorous certification process, robust construction, and inclusion of necessary sample conditioning hardware), to low, for sensors, though advanced research instruments can be equally expensive.
- **Operational and maintenance cost:** Ongoing maintenance and consumable expenses directly impact long-term data reliability and measurement uncertainty.

2.2.4 Regulatory acceptance

- **Ease of use:** Automation reduces operator-dependent error and measurement bias.
- **Multi-species capability:** The ability to measure multiple pollutants simultaneously from one sample.
- **Regulatory acceptance:** Confirms the entire measurement system, including sampling, calibration, and quality control, meets legally defensible standards for compliance purposes.

This unified evaluation framework enables optimal NO_x method selection by systematically comparing performance across analytical, applicability, operational, and regulatory criteria.

3. RESULTS

Using the critical evaluation parameters identified above, Table 5 summarizes the resulting performance data for each NO_x measurement method.

Table 5

Comparison matrix between methods.

Parameter	SRM	EQM	NSM
Accuracy	Definitive. Strict, legally defined bounds for bias and recovery.	Must be equivalent to SRM. Statistically demonstrated through field testing.	Uncertain/ Variable. Not validated against a regulatory standard.
Precision	Definitive. Strict, legally defined bounds for repeatability/ reproducibility.	Must be equivalent to SRM. Must meet the same statistical criteria.	Uncertain/ Variable. Highly dependent on instrument design and stability.
Selectivity/ specificity	High. The method is designed and tested to minimize interferences for its target analyte.	High. Must demonstrate no greater susceptibility to interferences than the SRM.	Variable. Can range from low (e.g., metal oxide sensors) to extremely high (e.g., research-grade MS).
Detection limit (LOD/ LOQ)	Defined in standard. Must be fit for purpose and meet minimum requirements.	Must be equivalent or better than SRM.	Variable. It can be ultra-sensitive (e.g., CRDS) or very high

Parameter	SRM	EQM	NSM
		Lower LOD is often a key advantage.	(e.g., low-cost sensors).
Suitability - Ambient air	Excellent. Designed specifically for this application.	Excellent. Performance is legally validated for this application.	Situational. May be suitable for screening or research but not compliance.
Suitability - Emissions	Excellent. Designed for harsh, high-concentration conditions.	Excellent. Performance is legally validated for stack monitoring.	Risky. May not withstand harsh conditions or have adequate range.
Measurement range	Legally defined. Optimized for expected concentrations (ppb for ambient, ppm for stack).	Must cover the SRM's range. Often extends beyond it, which is a benefit.	Highly variable. May not be optimized for the required application.
Time resolution	Defined in standard. (e.g., 1-hour average for ambient, 1-min for CEMS).	Must be equivalent to SRM. Often faster, which is a reported benefit.	Highly variable. Can be very fast (seconds) or very slow (integrated samples).
Portability	Typically, Low. Often rack-mounted or lab-based.	Variable. A key area for innovation (e.g., portable, solar-powered EQMs).	Variable. Includes both bulky research instruments and miniature sensors.
Initial capital cost	High (e.g., \$40k - \$100k+)	Moderate to High (e.g., \$20k - \$80k)	Very Low to Very High (e.g., \$100 - \$250k+)
Operational, maintenance cost	High (Requires strict QA/QC, specific consumables, expert technicians).	Often Lower (A key selling point; designed for lower maintenance and cost).	Variable. It can be very low (e.g., sensors) or extremely high (e.g., research MS).
Ease of use / Automation	Moderate. Highly automated but requires trained personnel for maintenance and QA.	High. A key advantage; often designed for simplicity and remote operation.	Highly Variable. From fully automated to entirely manual.
Multi-species capability	Typically, Low. Measures a single pollutant or a specific group (e.g., NO_x).	Typically, Low. Certified for a specific pollutant, though the platform may measure more.	Often High. Many research techniques (e.g., FTIR, PTR-MS) measure many compounds at once.
Regulatory acceptance	Full, Unconditional. The legal benchmark for compliance.	Full, Conditional. Accepted for compliance reporting upon successful designation.	None. Not acceptable for formal compliance or reporting.

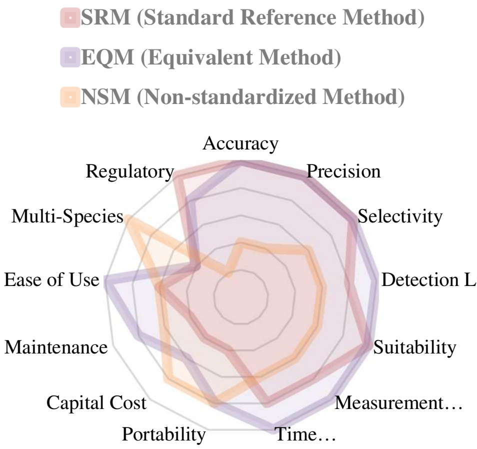

Fig. 1. The evaluation of methods.

Table 6

Key advantages and limitations of methods.

Method Category	Key Advantages	Key Limitations
Standard Reference Method (SRM): Chemiluminescence, UV Spectrophotometry, Alkaline-Permanganate/Colorimetric,	**1. Regulatory authority:** The legally definitive benchmark for compliance. Data is uncontestable in legal disputes. **2. Proven and defined performance:** Strict, legally enforceable specifications for accuracy, precision,	**1. Technological errors:** Can have inherent biases (e.g., CL converter inefficiency for NO_2, interferences in UV methods). **2. High cost:** Significant capital and operational costs (skilled maintenance, consumables, certified gases).

Method Category	Key Advantages	Key Limitations
Alkaline-Permanganate/IC	and interference rejection. **3. Standardized Operation:** Full, prescribed QA/QC protocols, calibration procedures, and data validation steps.	
Equivalent Method (EQM): Active DOAS, Portable FTIR, EC and Optical Sensors, MOS, Diffusive Sampling	**1. Regulatory acceptance:** Provides compliance-grade data for specific designated uses (e.g., path-integrated DOAS for area monitoring). **2. Operational flexibility:** Offers advantages like path-integrated measurement (DOAS), portability (FTIR), or time-integrated data (Diffusive Tubes). **3. Innovative validation:** Represents newer technologies that have met the high bar of equivalence testing.	**1. Conditional acceptance:** Equivalence is often granted for a specific application or concentration range, not universally. **2. Implementation complexity:** Methods like DOAS require careful placing and expertise to interpret path-averaged data. **3. Limited for NO_x:** Many EQM techniques (e.g., Diffusive Sampling) are better suited for VOCs or other pollutants than for NO_x.
Non-Standardized Method (NSM): Advanced Techniques (CAPS, CRDS, TDLAS, LIF, LOPAP) Low-Cost Sensors (LCS)	**A. Advanced techniques:** Often exceed SRMs in sensitivity, specificity (e.g., LOPAP), and speed. Enable discovery and measurement of new species and fast processes. **B. Low-cost sensors:** Enable hyperlocal mapping and citizen science at minimal cost. Ideal for leak detection, hotspot identification, and public engagement.	**A. Advanced techniques: High cost and complexity** (require expert operators and significant investment). **No regulatory status** (despite superior performance, lack official approval due to cost of validation). **B. Low-cost sensors: Poor data quality** (prone to severe drift, cross-sensitivities (e.g., NO_2 EC sensors to O_3), and environmental influence). **High data need** (require complex, ongoing calibration against reference methods; data is not regulatory grade).

Fig. 1 radar graph 1 provides a holistic comparison of the methods across all evaluation criteria. The analysis demonstrates a fundamental trade-off: no single method is universally optimal. SRMs ensure regulatory-grade data quality but lack scalability due to high cost and operational complexity. EQMs balance performance and practicality but offer limited multi-species capability and detection limits. NSMs provide exceptional portability and specificity but suffer from unreliable data and non-regulatory status. A hierarchical integration of these methods is therefore essential for comprehensive air quality assessment.

Building on this analysis, the application of the Trinitarian comparison model [31] further clarifies the core advantages and limitations of each method, detailed in Table 6.

This analysis clearly illustrates the core trade-offs: SRMs offer regulatory perfection but at a high cost, EQMs provide a balance of acceptance and flexibility, while NSMs offer either cutting-edge capability or widespread deployment potential, both outside the regulatory sphere.

3.1 Practical application and case studies

Comparative analysis of methods is best understood through the lens of real-world application, where monitoring objectives, environmental conditions, and resource constraints dictate the optimal choice. The following examples illustrate how the methods are deployed to solve specific air quality challenges.

- To map urban pollution hotspots and assess neighborhood-level exposure, a hybrid network combines a few reference-grade (SRM) analyzers [33] at 2-3 key locations for data credibility with a dense grid of low-cost (NSM) sensors. This synergy provides the high spatial resolution needed for detailed pollution mapping [34] at a feasible cost, which is impossible with sparse regulatory stations alone.
- For cost-effective long-term trend analysis and compliance checking of NO_2 in a rural area, passive samplers (EQM - EN 16339) [21], [36] are deployed across the region for 2–4-week periods. This method provides robust, spatially distributed data to establish a baseline, identify areas of concern, and justify the need for a permanent continuous monitor

if needed, avoiding the high cost of dense networks of automated stations.

- To address community concerns about fugitive emissions from a chemical plant, an open-path DOAS system (EQM - EN 16253) [20], [37] was deployed along the facility's perimeter. This technology directly quantifies the total pollutant crossing the fence line by measuring path-integrated concentrations over hundreds of meters, providing independent validation of emissions and distinguishing them from other sources like traffic.
- To study fast, low-concentration atmospheric processes like oxidation of NO_x to HONO, researchers use advanced analyzers (CRDS / LOPAP) [38] for their exceptional sensitivity and speed. These research-grade instruments provide the precise, high-resolution data needed to uncover chemical insights beyond the capabilities of standard regulatory monitors, ultimately improving atmospheric models.

3.2 Integration of multi-method data

A hierarchical framework integrates multi-method air quality data by using reference instruments (SRM/EQM) to calibrate dense networks of low-cost sensors (NSM). Through colocation and advanced algorithms, sensor data is corrected for drift and cross-sensitivities. In the urban case study, this process enabled a dense sensor network (~80 units) to achieve an R^2 of 0.82 with reference data after machine-learning calibration [39]. This integration revealed hyperlocal hotspots with 300% concentration variations invisible to the regulatory network alone [34], demonstrating how calibrated, multi-method data creates a spatially rich and scientifically robust picture that no single method can provide.

4. CONCLUSION

The study provides a comparative critical analysis of reference and alternative techniques for ambient nitrogen oxides (NO_x) measurement, evaluating their metrological performance, cost-effectiveness, and operational practicality to inform method selection for diverse monitoring objectives.

The novelty consists of:

- The monitoring paradigm: Replace single method approach with a hierarchical framework for Standard Reference Methods (SRM), Equivalent Methods (EQM), and Non-Standardized Methods (NSM) synergy.
- A method selection framework: A multi-criteria matrix for strategic method selection, balancing regulatory rigor, operational feasibility, and spatial resolution.
- Hierarchical data fusion: A formalized calibration pathway, using SRMs to validate scalable EQM/NSM networks for high-resolution, fit-for-purpose data.

Innovation in NO_x monitoring employs a strategic three-tiered framework. SRMs provide the metrological foundation for regulatory compliance and legal defensibility. Concurrently, EQMs and advanced NSMs enable network densification, delivering the spatial / temporal resolution for hyperlocal mapping and atmospheric research.

The principal impediment is systemic, necessitating the development of universal validation protocols, compensation for sensor cross-sensitivities, and the implementation of robust data fusion architectures. The innovation is a standardized hierarchical calibration framework, which integrates these methodological levels, to produce multi-scale air quality data, that is both scientifically defensible and policy relevant.

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Analiză critică a metodelor inovatoare și clasice pentru analiza oxizilor de azot din aerul înconjurător

Acest studiu prezintă o analiză critică comparativă a metodelor de referință și a celor alternative, utilizate pentru măsurarea oxizilor de azot (NO_x) în mediul ambiant. Studiul evaluează sistematic tehnicile consacrate, cum ar fi chemiluminiscența, alături de noile alternative, inclusiv senzorii spectroscopici și dispozitivele de eșantionare pasivă. Lucrarea evidențiază punctele forte și limitele fiecărei metode, concentrându-se pe performanța metrologică, rentabilitatea și caracterul practic operațional în cadrul rețelelor de monitorizare la scară largă. Constatările relevă un compromis între precizia metodelor de referință și fezabilitatea extinsă a abordărilor alternative. În cele din urmă, această analiză oferă un cadru pentru selectarea celei mai potrivite metodologii, pe baza obiectivelor de monitorizare, a disponibilității resurselor și a calității necesare a datelor.

Venera-Stanca NICOLICI, PhD student, Politehnica University Timisoara, Faculty of Mechanical Engineering, MMUT, venera-stanca.morar@student.upt.ro, Timisoara, Romania

Ahmed ADJAL, PhD student, Politehnica University Timisoara, Faculty of Mechanical Engineering, MMUT, ahmed.adjal@student.upt.ro, Timisoara, Romania

Ioana IONEL, PhD, Professor, Politehnica University Timisoara, Faculty of Mechanical Engineering, MMUT, ioana.ionel@upt.ro, Timisoara, Romania