

New calibrations for estimating the N/O ratio in H II regions

Estrella Florido,^{1,2★} Almudena Zurita^{1,2} and Enrique Pérez-Montero³

¹*Departamento de Física Teórica y del Cosmos, Campus de Fuentenueva, Edificio Mecenas, Universidad de Granada, E-18071 Granada, Spain*

²*Instituto Carlos I de Física Teórica y Computacional, Facultad de Ciencias, Universidad de Granada, E-18071 Granada, Spain*

³*Instituto de Astrofísica de Andalucía, Camino Bajo de Huétor s/n, Aptdo. 3004, E-18080 Granada, Spain*

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ABSTRACT

We use a sample of 536 H II regions located in nearby spirals, with a homogeneous determination of their T_e -based abundances, to obtain new empirical calibrations of the N2O2, N2S2, O3N2, and N2 strong-line indices to estimate the nitrogen-to-oxygen abundance ratio when auroral lines are not detected. All indices are strongly correlated with the T_e -based $\log(N/O)$ for our H II region sample, even more strongly than with $12 + \log(O/H)$. N2O2 is the most strongly correlated index, and the best fit to the $\log(N/O)$ –N2O2 relation is obtained with a second-order polynomial. The derived relation has a low dispersion (rms < 0.09 dex), being valid in the range $-1.74 < \text{N2O2} < 0.62$ (or $-1.81 < \log(N/O) < -0.13$). We have compared our calibration with previous ones and have discussed the differences between them in terms of the nature of the objects used as calibrators.

Key words: ISM: abundances – (ISM:) H II regions – galaxies: abundances – galaxies: ISM – galaxies: spiral.

1 INTRODUCTION

Most of the chemical elements heavier than hydrogen and helium are formed by stars, which, at different stages of their evolution, expel part of them into the interstellar medium (ISM), enriching it with *metals*. The metal content in a galaxy changes with time depending on its overall star formation, but also on processes such as gas inflows of pristine gas or gas outflows and stripping, that alter the metal concentration relative to hydrogen. Therefore, the current chemical composition and the distribution of metals in the ISM of galaxies, provide crucial pieces of information to the key physical processes driving galaxy evolution (e.g. Maiolino & Mannucci 2019). For this reason, oxygen, the most abundant metal in the Universe, has been extensively used as a tracer of the *metallicity* or $12 + \log(O/H)$ in the gas-phase of galaxies (e.g. Searle 1971; Pagel, Edmunds & Smith 1980; Bresolin, Garnett & Kennicutt 2004; Kewley et al. 2010; Pilyugin, Grebel & Kniazev 2014; Bresolin 2019). Oxygen is a primary element (its yield is independent of the initial chemical composition of the star), being produced by massive stars and ejected into the ISM in a short time-scale via the explosion of Type II supernovae, a few Myr after the star was formed, thus increasing the O/H ratio in the ISM.

In addition to O/H, other abundance ratios such as N/O are key tools to understand chemical evolution in galaxies. However, nitrogen production is much more complex than oxygen production, as it is produced in stars of all masses and it can have both primary and secondary origins (e.g. Edmunds & Pagel 1978; Gavilán, Mollá & Buell 2006; Vincenzo et al. 2016). It is produced from C and O through the CNO cycle for the combustion of H in He, being most of it (~74 per cent) produced in low- and intermediate-mass stars (LIM stars, $\lesssim 8 M_\odot$), according to chemical evolution models (e.g.

Matteucci 1986; Chiappini, Romano & Matteucci 2003; Kobayashi, Karakas & Lugaro 2020). The mean lifetimes of LIM stars are longer than those of more massive stars and, therefore, there is a time delay in the enrichment of nitrogen in the ISM with respect to that of oxygen. The N/O abundance ratio of the ISM in a galaxy would then be sensitive to the age of the galaxy, or to the time since most of its star formation has taken place, in the extreme case where all the star formation occurs in a single burst from the galaxy's gas (single stellar population) (e.g. Edmunds & Pagel 1978). A more realistic scenario for spiral and irregular galaxies implies a continuous star formation that makes the N/O abundance ratio very sensitive to their star-formation history and efficiency (Mollá et al. 2006; Vincenzo et al. 2016).

The most commonly used metallicity indicators in the ISM, the O/H and N/O abundance ratios, are therefore complementary, with O/H being more fickle, more dependent on intermittent pollution by short-lived massive stars following star-formation (hereinafter, SF) bursts, and modulated by the inflows and outflows of pristine gas, while N/O is less sensitive to gas flows and more sensitive to the SF history of the galaxy or the H II region (e.g. Köppen & Hensler 2005; Mollá et al. 2006; Vincenzo et al. 2016). Indeed, an important diagnostic tool for constraining both chemical evolutionary processes and the origin of nitrogen is the O/H–N/O diagram, either for individual H II regions (e.g. Alloin et al. 1979; Considère et al. 2000; Henry, Edmunds & Köppen 2000; Belfiore et al. 2017; Arellano-Córdova et al. 2021), as well as for all or part of the integrated light emitted by galaxies (e.g. Amorín, Pérez-Montero & Vílchez 2010; Andrews & Martini 2013; Vincenzo et al. 2016; Loaiza-Agudelo, Overzier & Heckman 2020; Luo et al. 2021). In particular, our current improved observation capabilities, have permitted us to derive average O/H and N/O estimates for high-redshift galaxies, that compared with local estimates constrain the current theories about galactic evolution, or suggest new scenarios for that evolution (e.g. Pérez-Montero et al. 2013, 2021; Masters

* E-mail: estrella@ugr.es

et al. 2014; Sanders et al. 2018; Vangioni et al. 2018; Maiolino & Mannucci 2019).

The gas-phase N/O abundance ratio of galaxies has been found to correlate positively with the stellar mass of the galaxy (e.g. Pérez-Montero & Contini 2009; Pérez-Montero et al. 2013), as does the gas-phase O/H in the so-called mass–metallicity relation (e.g. Tremonti et al. 2004). However, there are contradictory results regarding the dependence of the N/O– M_* relation on the star-formation rate (SFR). According to Pérez-Montero et al. (2013), it is independent of SFR, unlike O/H, but more recent results from Hayden-Pawson et al. (2022) find the same anticorrelation of N/O with SFR as O/H. Hayden-Pawson et al. (2022) explain the observed discrepancies, that can have important consequences for explaining the processes driving the fundamental metallicity relation, as due to the choice of the empirical diagnostic used to derive N/O (N2S2 versus N2O2; Hayden-Pawson et al. 2022).

Another advantage of N/O with respect to O/H is that the former has little dependence on the gas electron temperature, T_e , as it is derived from a pair of collisionally excited lines ([O II] λ 3726,3729 and [N II] λ 6583) whose emissivities have similar dependence on T_e (e.g. Skillman 1998), and it is also one of the most robust abundance relations against ionization correction factors to account for unobserved ionic species (e.g. Stasińska 2002; Esteban & García-Rojas 2018; Arellano-Córdova & Rodríguez 2020).

Although it is not without problems (e.g. Stasińska 2002; Bresolin 2008), the so-called *direct* or T_e -based method¹ (e.g. Bresolin et al. 2004; Pérez-Montero 2014a; Berg et al. 2020) is considered the most accurate for determining the O/H and N/O abundance ratios in H II regions or in the gas-phase of galaxies. The drawback is that it requires the detection of very faint collisionally excited emission lines, known as *auroral* lines, which allow the estimation of T_e , a necessary step to determine the corresponding ionic abundance. The detection of the auroral lines is more complicated at high metallicities, as an increase in metallicity has the effect of increasing the cooling in the nebula, and the relevant emission-line ratios remain unreachable even for 10 m class telescopes (Bresolin 1996). An alternative method is that based on measurements of optical metal recombination lines, where the line emissivities are only moderately dependent on T_e , but these lines are very faint and only detectable in the Milky Way and nearby galaxies (e.g. García-Rojas et al. 2006; Toribio San Cipriano et al. 2016; Esteban et al. 2020).

These observational limitations have motivated the use of *strong-line* methods, first introduced by Pagel et al. (1979), as an alternative to estimate the gas-phase oxygen abundance when auroral lines and/or optical metal recombination lines cannot be detected. These methods are based on the calibration of ratios of strong and easily detectable emission lines of the nebula. The strong-line ratios are typically calibrated either using T_e -based metallicities (e.g. Pettini & Pagel 2004; Bresolin 2007; Marino et al. 2013; Pilyugin & Grebel 2016) or metallicities predicted with photoionization models (PhM; e.g. McGaugh 1991; Kewley & Dopita 2002; Dopita et al. 2016). Both PhM and methods based on metal recombination lines tend to estimate larger oxygen abundances than the T_e method (e.g. Bresolin et al. 2009; Esteban, Toribio San Cipriano & García-Rojas 2018; Zurita et al. 2021a) but see also Dors et al. (2011) and Pérez-Montero (2014a).

Strong-line methods for the derivation of O/H (metallicity) are extremely popular, and a high number of different calibrations and

methods are available in the literature (see e.g. Maiolino & Mannucci 2019, for a compilation). Although these methods are less precise than the T_e -based method, they have been extremely useful for making metallicity estimates for large sets of H II regions or star-forming sites (e.g. Sánchez-Menguiano et al. 2018; Zurita et al. 2021a) or for distant galaxies, especially at high redshift, where usually only a few emission lines are detected (e.g. Brown, Martini & Andrews 2016; Dopita et al. 2016), leading to important results and scaling relations (e.g. Tremonti et al. 2004).

Despite its relevance, the number of available strong-line methods for the derivation of N/O is much scarcer than those for O/H, and the ones available have not been as carefully tested as those to derive O/H. In the derivation of empirical strong-line methods, there are some minimum requirements, important for a reliable calibration which are related to the properties of the calibration sample: (1) It must comprise a large number of objects with T_e -based abundances, (2) the methodology to derive abundances for all the targets must be homogeneous, and (3) the calibration targets must cover a wide range of abundances and/or strong-line index values.

The aims of this work (TW) are to analyse some of the most frequently used strong-line methods to estimate the N/O abundance ratio in H II regions and in the gas-phase of star-forming galaxies in the literature, and to derive new empirical strong-line methods to estimate N/O. We will make use of the recent compilation of emission-line fluxes for H II regions in nearby galaxies done by Zurita et al. (2021a), for investigating the effect of galactic bars on the gas-phase abundance gradients of spirals (Zurita et al. 2021b).

This paper is organized as follows. In Section 2, we summarize the H II region sample properties. In Section 3, we first analyse the strong-line ratios or indices that are suitable candidates to be indicators of the N/O abundance ratio in H II regions, and then explore their dependence with second-order parameters. The comparison of our new empirical calibrations to derive N/O with previous methods is presented in Section 4. We discuss the results in Section 5 and, finally, present our conclusions in Section 6.

2 H II REGION SAMPLE

This work is based on a large sample of H II regions for which emission-line fluxes were available in the literature and compiled by Zurita et al. (2021a). The sample comprises 2831 independent measurements of H II regions² from 51 nearby (<64 Mpc) spiral galaxies with absolute B -band magnitudes between -22 and -17 , and inclinations lower than 70° .

The compilation comprises celestial coordinates and emission-line fluxes, including those from auroral lines, when available in the original papers. The latter permitted the derivation of O/H and N/O abundance ratios with the T_e -based or *direct* method for 610 and 536 H II regions, respectively, with a homogeneous methodology³. The *direct* abundances range from 7.42 to 9.07 for $12 + \log(\text{O/H})$, and from -1.81 to -0.13 for $\log(\text{N/O})$.

²Some of these measurements correspond to the same H II region, but observed by different authors. All different observations of the same target were kept as independent observations.

³The collected emission-line fluxes are not homogeneous, as they come from previous publications by different authors. However, we concentrated our collection on resolved spectroscopic data of H II regions, and we estimated that the differences in the emission-line fluxes for a given region, as measured by different authors, are not larger than the typical observational error associated to emission-line flux measurements (see Section 3.1 in Zurita et al. 2021a).

¹Throughout this paper we will refer to the abundances obtained by this method indistinctly as *direct* or T_e -based abundances.

We refer the reader to Zurita et al. (2021a) for details on the galaxy and H II region sample, and on the methodology to derive the chemical abundances from the compiled emission-line fluxes.

In this paper we take advantage of this compilation with a double purpose: (1) to analyse some of the most frequently used strong-line methods to estimate the N/O abundance ratio in H II regions and in the gas-phase of star-forming galaxies, and (2) to derive new empirical strong-line methods for the derivation of N/O in H II regions. Our calibrating sample comprises the 536 H II regions for which the T_e -based N/O abundance ratio was derived in Zurita et al. (2021a). This calibrating sample has the advantage of uniformity, as it is composed by H II regions within spiral galaxies alone, in contrast with previous samples that included H II regions from different galaxy types and/or integrated fluxes from galaxies (e.g. Liang et al. 2006; Pérez-Montero & Contini 2009; Pilyugin, Grebel & Mattsson 2012).

3 STRONG-LINE RATIOS TO DERIVE N/O

The difficulties for detecting reliably the faint auroral lines needed for the determination of T_e , motivated the development of alternative methods to estimate chemical abundances from strong nebular emission lines. The most widely used methods involve fluxes from the [N II] λ 6583, [O III] λ 5007, [O II] λ 3727, and/or [S II] λ 6717,6731 emission lines, besides the H α and H β Balmer series lines, as these are easily detected in the optical range in spectroscopic observations of nearby galaxies with medium-size telescopes from Earth. The number of different strong-line ratios and calibrations for the derivation of O/H is enormous, while this number is much limited for the derivation of N/O (see e.g. Maiolino & Mannucci 2019, for a review). One of the drawbacks of some of the strong-line methods in use for deriving O/H, is their dependence on other parameters (density, ionization parameter, etc.). In particular, those including the [N II] λ 6583 emission line introduce a dependence of the O/H derived abundances with the N/H or N/O abundance ratio (e.g. Pérez-Montero & Díaz 2005; Pérez-Montero & Contini 2009; Zurita et al. 2021a).

We have selected some of the most widely used metallicity strong-line indices that include in their definition the [N II] λ 6583 emission-line flux:

- (i) N2 = $\log ([\text{N II}]\lambda 6583/\text{H}\alpha)$,
- (ii) O3N2 = $\log ([\text{O III}]\lambda 5007/\text{H}\beta)/([\text{N II}]\lambda 6583/\text{H}\alpha)$,
- (iii) N2O2 = $\log ([\text{N II}]\lambda 6583/[\text{O II}]\lambda 3727)$, and
- (iv) N2S2 = $\log ([\text{N II}]\lambda 6583/[\text{S II}]\lambda 6717,6731)$.

The N2, O3N2, and N2O2 indices are widely used for the derivation of O/H (see e.g. Shapley et al. 2005; Ho et al. 2015; Sánchez-Menguiano et al. 2018, respectively). The N2 index (Storch-Bergmann, Calzetti & Kinney 1994; Denicoló, Terlevich & Terlevich 2002) has the advantage of using very close-by lines in the spectra, which minimizes the effect of differential dust extinction and requires a very small spectral coverage in observations, but it has the disadvantages that it saturates at high metallicity (Baldwin, Phillips & Terlevich 1981), its behaviour is not linear at low metallicities (Morales-Luis et al. 2014), and it depends strongly on the ionization parameter (e.g. Pérez-Montero & Díaz 2005). O3N2 was first proposed by Alloin et al. (1979), and it is a very popular method for deriving oxygen abundances, since it is also useful in surveys with limited spectral coverage, although it is strongly dependent on the H II region ionization parameter (e.g. Ho et al. 2015; Zurita et al. 2021a) and it saturates at low-oxygen abundances values ($12 + \log(\text{O}/\text{H}) \lesssim 8$; Pérez-Montero & Contini 2009).

Table 1. Spearman’s rank correlation coefficient (ρ) for both the T_e -based $\log(\text{N}/\text{O})$ and $12 + \log(\text{O}/\text{H})$ abundances as a function of the four selected indices. N is the number of H II regions used in each inspected relation.

Index	$\log(\text{N}/\text{O})$		$12 + \log(\text{O}/\text{H})$	
	N	ρ	N	ρ
N2	536	0.88	544	0.55
O3N2	530	−0.85	538	−0.56
N2O2	536	0.95	544	0.62
N2S2	530	0.78	538	0.58

The N2S2 index also makes use of close-by in wavelength emission lines, but it considers the [S II] λ 6717,6731 doublet, which is fainter and therefore more difficult to detect. It was first proposed as a metallicity indicator for H II regions by Viironen et al. (2007), and later on by Dopita et al. (2016) for high-redshift galaxies. Pérez-Montero & Contini (2009) proposed it as an indicator of the N/O ratio on ionized nebulae. The N2O2 index, suggested by Kewley & Dopita (2002), is the one most affected by differential extinction and by flux calibration uncertainties, but it is a frequently used metallicity indicator for H II regions with $12 + \log(\text{O}/\text{H}) \gtrsim 7.6$ (Dopita et al. 2000), and it is also a useful tool to derive the N/O abundance ratio (Pérez-Montero & Contini 2009). Both N2O2 and N2S2 are virtually independent on the ionization parameter (e.g. Dopita et al. 2000; Nagao, Maiolino & Marconi 2006; Zurita et al. 2021a).

The strengths, weaknesses, and caveats of the use of these indices for the derivation of metallicities have been widely discussed in the aforementioned references and/or evaluated against the more reliable T_e -based method, and to a much lesser degree for the derivation of N/O (see also Pérez-Montero & Díaz 2005; Kewley & Ellison 2008; López-Sánchez & Esteban 2010; Maiolino & Mannucci 2019; Arellano-Córdova et al. 2020; Zurita et al. 2021a).

We have used our sample of H II regions (Section 2) to analyse the relation between the N2, O3N2, N2O2, and N2S2 indices and the T_e -based N/O abundance ratio. As a first step, we derive the Spearman’s rank correlation coefficient (ρ) between the H II region values for each index, and the corresponding T_e -based $\log(\text{N}/\text{O})$ abundance ratio. The results are shown in Table 1, together with the number of data values (N) involved in each relation. All indices show a strong correlation with $\log(\text{N}/\text{O})$, with values of ρ greater than 0.78, but the strongest correlation is found for the N2O2 index, with $\rho = 0.95$. For comparison, we show in the same table the correlation coefficient of the same indices with the T_e -based oxygen abundance, for which they are more widely used. The Spearman’s rank correlation coefficient for $12 + \log(\text{O}/\text{H})$ is lower than for $\log(\text{N}/\text{O})$, indicating moderate correlations, with ρ values around 0.6 for all indices.

In the next subsections we further explore the use of the four strong-line indices as indicators of $\log(\text{N}/\text{O})$ for our H II region sample, with more emphasis on the N2O2 index that shows the strongest correlation with the T_e -based nitrogen-over-oxygen abundance ratio.

3.1 N2O2

Fig. 1 shows the $\log(\text{N}/\text{O})$ abundance ratio derived from the T_e -method against the N2O2 index. Individual H II region values are indicated with black dots. An underlying density map for the same data set is shown in red colours, which allows a better inspection of the distribution in areas of the plot with a high overlapping of data points (darker red).

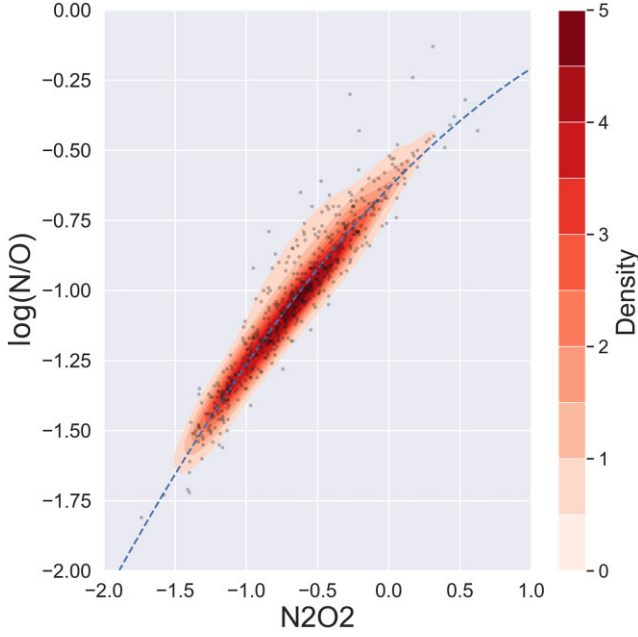


Figure 1. $\log(N/O)$ for H II regions as derived from the *direct* method (Zurita et al. 2021a) versus the N2O2 index. Both individual data points (black dots) and a density map from the same data set are shown. The dashed-blue line shows the best fit to the data points (see text for details). Typical uncertainties in $\log(N/O)$, not plotted for clarity, are ~ 0.17 dex.

We have derived the function that best fits the T_e -based $\log(N/O)$ –N2O2 relation. Several fitting techniques have been explored that include the use of Bayesian statistical methods, weighted/unweighted fits considering uncertainties in both parameters, the use of different degrees in the polynomial fitting, and/or the derivation of the best-fitting function for average values within N2O2 and $\log(N/O)$ bins, rather than for the individual data points. For a first evaluation of the goodness of the fit we have calculated the median value of the fitting residuals and their standard deviation.

The best-fitting function to the data is a second-order polynomial, with weights equal to the reciprocal of the squared uncertainties in $\log(N/O)$ and yields

$$\log(N/O)_{N2O2} = (-0.102 \pm 0.018) \times N2O2^2 + (0.528 \pm 0.019) \times N2O2 - (0.634 \pm 0.006). \quad (1)$$

It is shown with a blue dashed line in Fig. 1. The median value of the residuals is 0.002 ± 0.004 dex and their standard deviation is 0.085 dex. A careful analysis of the fitting residuals is shown in the top panels of Fig. 2 where these are plotted as a function of the N2O2 index, the T_e -based metallicity, the T_e -based $\log(N/O)$, and $\log O_{32}$ ($=\log([O III]\lambda\lambda 4959, 5007/[O II]\lambda 3727)$) as a proxy for the ionization parameter in the H II regions. It can be clearly seen that the residuals from our fit (equation 1) show a positive correlation with the T_e -based oxygen abundance, whereas no correlation is observed with either the T_e -based $\log(N/O)$ or $\log O_{32}$.

In order to correct for this, we have tested a new fitting function taking into account both the N2O2 index and the T_e -based O/H abundance as independent variables, and using the reciprocal of the squared uncertainties in $\log(N/O)$ as weights. The resulting function

is

$$\log(N/O)_{\text{cor}} = (-0.160 \pm 0.011) \times N2O2^2 + (0.59 \pm 0.02) \times N2O2 + (2.20 \pm 0.08) - (0.330 \pm 0.009) \times (12 + \log(O/H)). \quad (2)$$

The fitting residuals from equation (2) are shown in the bottom panels of Fig. 2. There are no significant dependencies of the residuals with the oxygen abundance or the ionization parameter of the H II regions. The dispersion of the residuals has been reduced with the fitting of equation (2) from 0.085 to 0.041 dex. Their median value is however slightly higher now than with the fitting from equation (1), -0.004 ± 0.002 dex, but both values are comparable if we consider error bars, and are, in any case, smaller than the data dispersion.

The improvement reached with this new fitting in terms of the reduction of residuals dispersion and its dependence on the T_e -based $12 + \log(O/H)$ is better seen in Fig. 3, where we plot the residuals from the two best-fitting lines (equations 1 and 2) as a function of the N2O2 parameter with yellow triangles and black dots, respectively. It is important to note that although equation (2) yields a better fitting to the data, the empirical calibration of N2O2 to derive $\log(N/O)$ given in equation (1) is already very good. Equation (2) requires knowledge of the T_e -based $12 + \log(O/H)$. Its usefulness is then limited to cases where the electron temperature and the *direct* oxygen abundance can be determined, but the N/O abundance ratio cannot be derived, presumably in limited spectral range observations, which do not include the $[N II]\lambda 6583$ emission line. However, even for these objects, equation (1) would already yield a rather acceptable estimation of $\log(N/O)$. In fact, the mean (0.0002 dex) and median (-0.008 dex) difference in the $\log(N/O)$ values derived from equations (1) and (2) are much smaller than the typical median values (0.17 dex) of the uncertainties in the T_e -based $\log(N/O)$ abundances for the H II regions in our sample.

The range of validity of the two fittings, the number of H II regions used for these empirical calibrations of N2O2, and the median value and the standard deviation of the fitting residuals are summarized in the first two lines of Table 2.

3.2 N2S2, O3N2, and N2

The N2S2, O3N2, and N2 indices are widely used for the derivation of metallicities. However, although these indices are less strongly correlated with $\log(N/O)$ than N2O2 (Table 1), their correlation with N/O is also strong ($\rho \sim 0.78$ – 0.88) and, in any case, much stronger than their correlation with $12 + \log(O/H)$, with $\rho \sim 0.55$ – 0.58 . We explore here the usefulness of N2S2, O3N2, and N2 as empirical indicators of N/O in our H II region sample. Fig. 4 shows T_e -based $\log(N/O)$ abundances from Zurita et al. (2021a) as a function of N2S2, O3N2, and N2. The figure shows, as a first approach, the best linear fittings (blue straight lines). The dispersion of the fitting residuals is slightly worse for N2S2 (~ 0.19 dex) than for O3N2 and N2 (~ 0.14 dex), but the median value for the residuals is very close to zero (-0.004 dex).

The O3N2 and N2 indices are known to be strongly dependent on the H II region ionization parameter (e.g. Pérez-Montero & Díaz 2005; Pérez-Montero & Contini 2009; López-Sánchez et al. 2011; Marino et al. 2013, and references therein). In fact, we have seen this dependence for the residuals of the best-fitting straight lines shown in Fig. 4. Therefore, we have performed a second fitting of T_e -based $\log(N/O)$ values for the H II regions of our sample as a function of two independent variables: the index (either O3N2 or N2) and $\log(O_{32})$, the later as a proxy for the ionization parameter.

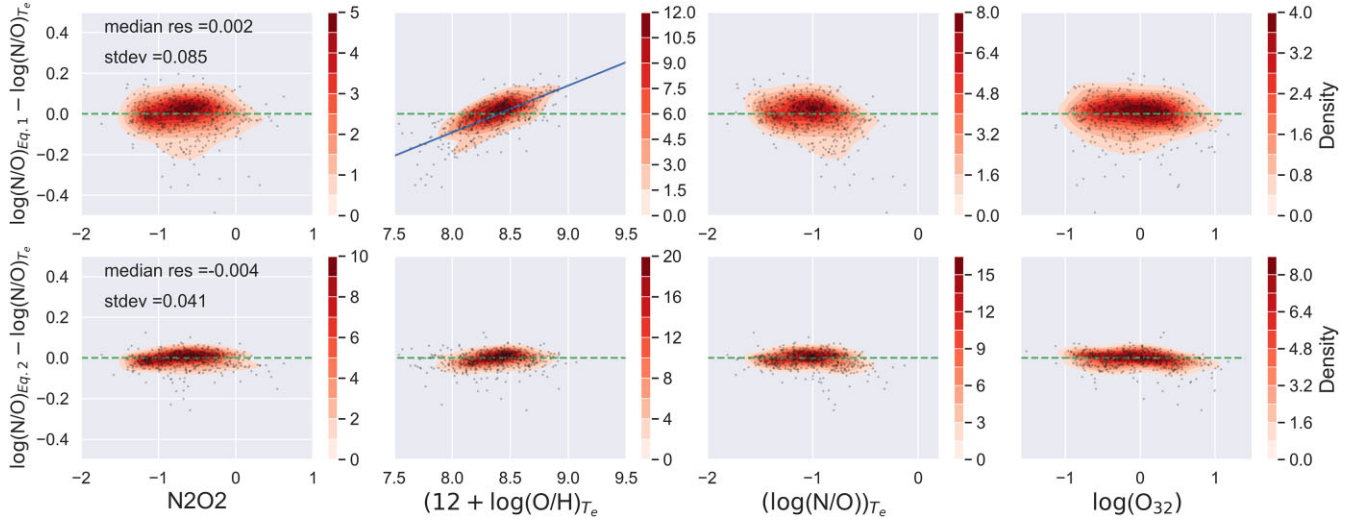


Figure 2. Difference between the N/O abundances derived from our best fitting and the corresponding T_e -based value (residuals) as a function of the N2O2 index, the T_e -based O/H and N/O abundances, and $\log O_{32}$, for the best fitting in equation (1) and equation (2) in the top and bottom panels, respectively. An underlying density map for the same data set is shown in red colours in addition to the individual data points (black dots). The median value of the residuals and their standard deviation for each fitting is indicated in the corresponding left-hand panel. The green-dashed straight line marks the zero residuals line. The blue straight line shows the linear correlation between the residuals from equation (1) and the T_e -based $12 + \log(O/H)$.

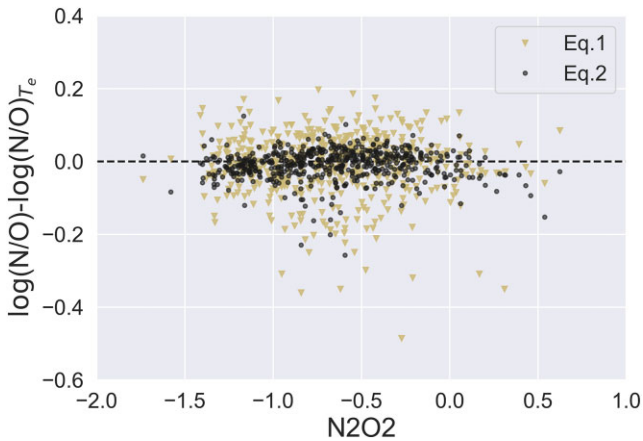


Figure 3. Fitting residuals for the two empirical calibrations of the N2O2 index for the derivation of $\log(N/O)$, as a function of N2O2 for our H II region calibrating sample. Yellow triangles and black dots correspond to residuals from the fitting functions in equations (1) and (2), respectively.

The resulting fits reduce considerably the dispersion of the residuals down to ~ 0.09 dex for the two indices, while the median value for the residuals remains similar for O3N2 as for the previous fitting, and is reduced down to -0.003 dex for N2. As N2 saturates at high abundances ($N2 \gtrsim -0.6$), in Fig. 4 we have restricted the fitting to H II regions with N2 values in the range $-1.5 < N2 < -0.65$ (294 out of 536 regions).

Table 2 shows the best-fitting parameters for the $\log(N/O)$ in our H II region sample as a function of the different strong-line ratios (N2O2, N2S2, O3N2, and N2), including those for the fits considering second-order dependencies on $12 + \log(O/H)$, for N2O2, and on $\log(O_{32})$ for O3N2 and N2. The range of validity of the different empirical calibrations of these indices for the derivation of $\log(N/O)$ is also given.

In summary, the four indices show a strong correlation with $\log(N/O)$. Our best-fitting functions to the T_e -based H II region N/O

abundances indicate that N2O2 is the best tracer of N/O, given the small dispersion of the fitting residuals and the relatively wide range of validity for this empirical calibration. O3N2 and N2 also show a small dispersion when their dependence on the ionization parameter is taken into account, but their range of validity is smaller, especially for N2.

4 COMPARISON WITH PREVIOUS STRONG-LINE CALIBRATIONS FOR N/O ESTIMATES

We have made a rather exhaustive, although possibly not complete, compilation from the literature of the most recent and frequently used methods to derive the gas-phase N/O abundance ratio. We have paid especial attention to the type of calibrating objects and to the ranges of validity for each analysed method. All of them, in addition to our derived calibrations, appear in Table 3, where we also show the most relevant pieces of information for each of these methods.

In the following subsections we will carefully compare all the collected methods with our derived strong-line calibrations (Section 3) to estimate $\log(N/O)$. Our comparison will be based on two elements: (1) the derived empirical parametrizations, and (2) the standard deviation and the median value of the difference between the T_e -based $\log(N/O)$ values and those obtained from each strong-line method for our H II region sample (columns 7 and 8 in Table 3).

4.1 Methods based on the N2O2 index

N2O2 is the most commonly used index for estimating the ionized gas-phase N/O abundance ratio. Some of the most frequently used calibrations of this index derived by previous work are summarized in the top rows of Table 3. Their corresponding analytical expressions have been used to overplot them in Fig. 5, on the $\log(N/O)$ versus N2O2 diagram for our H II region sample.

Except for the calibration performed by ST18 and LS15, respectively, all the rest have been obtained empirically from determinations

Table 2. Best-fitting parameters to the T_e -based $\log(N/O)$ as a function of the strong-line indices N2O2, N2S2, O3N2, and N2, for the empirical calibrations derived in this work. Columns (1) and (2) show the independent variables for the fitting; column (3) resulting empirical calibration; column (4) validity range for the calibration given in column (3); column (5) Spearman’s rank correlation coefficient between $\log(N/O)$ and the strong-line index in column 1, x_1 , in this index range; column (6) standard deviation; column (7) median value of the fitting residuals; and column (8) shows the number of H II regions used in each fitting. Note that the number of H II regions used for the calibration of the N2 index is much smaller than for the other indices, due to its reduced range of validity.

x_1	x_2	$\log(N/O) =$	Validity range (dex)	ρ	Residuals stdev (dex)	Median residuals (dex)	N
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
N2O2	–	$(-0.102 \pm 0.018)x_1^2 + (0.528 \pm 0.019)x_1 - (0.634 \pm 0.006)$	$-1.74 < x_1 < 0.62$	0.95	0.085	0.002	536
N2O2	$12 + \log(O/H)$	$(-0.16 \pm 0.01)x_1^2 + (0.59 \pm 0.02)x_1 + (2.20 \pm 0.08) - (0.330 \pm 0.009)x_2$	$-1.74 < x_1 < 0.62$	0.95	0.041	-0.004	536
N2S2	–	$(0.84 \pm 0.03)x_1 - (1.071 \pm 0.008)$	$-0.58 < x_1 < 0.84$	0.78	0.19	-0.004	530
O3N2	–	$(-0.28 \pm 0.01)x_1 - (0.77 \pm 0.01)$	$-1.61 < x_1 < 2.86$	-0.85	0.15	0.03	530
O3N2	$\log(O_{32})$	$(-0.73 \pm 0.01)x_1 - (0.29 \pm 0.02) + (0.74 \pm 0.02)x_2$	$-1.61 < x_1 < 2.86$	-0.85	0.09	0.025	530
N2	–	$(0.71 \pm 0.04)x_1 - (0.48 \pm 0.04)$	$-1.5 < x_1 < -0.65$	0.74	0.13	0.014	294
N2	$\log(O_{32})$	$(0.85 \pm 0.03)x_1 - (0.40 \pm 0.03) + (0.33 \pm 0.02)x_2$	$-1.5 < x_1 < -0.65$	0.74	0.09	-0.003	294

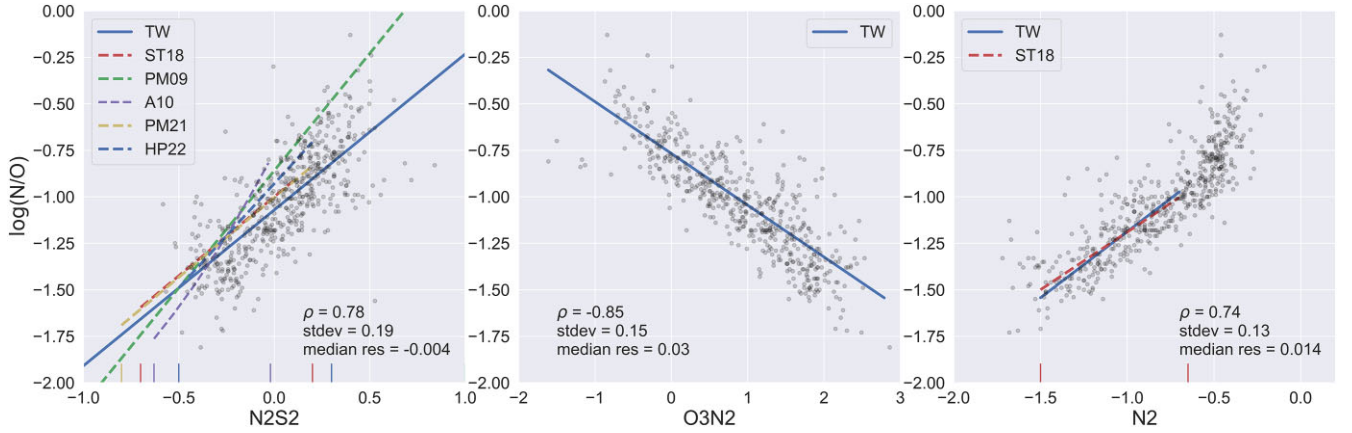


Figure 4. T_e -based $\log(N/O)$ abundance ratio versus the strong-line ratios N2S2, O3N2, and N2. The blue straight line shows our best linear fitting to the data (TW). The Spearman’s rank correlation coefficient is shown in the bottom part of the plots, together with the standard deviation and median value of the fitting residuals. Calibrations of these indices obtained by Strom et al. (2018), Pérez-Montero & Contini (2009), Amorín et al. (2010), Pérez-Montero et al. (2021), and Hayden-Pawson et al. (2022) are shown in the corresponding panels with green, red, purple, yellow, and blue dash lines, respectively. Vertical segments in the bottom part of the panels indicate the validity range limits for each calibration, with the corresponding colour. The blue straight line in the right-hand panel shows the best fitting (TW) obtained for the N2 index for values of N2 between -1.5 and -0.65 . See text for details.

of the N/O abundance ratio from the T_e -based method. However, the nature of the targets used as calibrators changes from one calibration to another. The analytical calibrations by LS15 and ST17, are the only ones based exclusively on H II regions. The calibration by LS15 is obtained from N/O abundances derived from an empirical determination of the T_e for 48 H II regions of the galaxy pair NGC 1510/NGC 1512, with N2O2 values in the range of -1.45 to 0.15 dex, very similar to the range covered by our data sample. Their empirical calibration departs (≤ 0.18 dex) from ours only for low values of N2O2 (≤ -1.3 dex). The median difference between T_e -based $\log(N/O)$ and the $\log(N/O)$ values derived from the LS15 calibration for our H II region sample is 0.04 dex, with a standard deviation of 0.09 dex, very similar to the dispersion of the residuals for our calibration (equation 1).

The ST17 calibration is derived from a considerably larger sample than in LS15, and contains 414 extragalactic H II regions collected by

Pilyugin et al. (2012), of which only 105 belong to spiral galaxies⁴ and the rest are from irregular galaxies. As we can see in Fig. 5, the ST17 calibration almost matches the one performed in TW (equation 1) in the range $-0.8 \leq N2O2 \leq -0.3$ dex, finding the largest difference between ours and ST17’s calibration at the highest and lowest values of N2O2. However, this difference is small, ≤ 0.15 – 0.20 dex. The comparison between ST17’s and our empirical calibration is better seen in Fig. 6, where the Pilyugin et al. (2012) H II region sample employed by ST17 is also plotted, with blue squares and red dots for H II regions from irregular and spiral galaxies, respectively. We can see that there are less than 10 H II regions in their calibrating sample with N2O2 greater than

⁴All the H II regions belonging to spiral galaxies in the Pilyugin et al. (2012) sample are included in the Zurita et al. (2021a) H II region sample used in this paper.

Table 3. List of strong-line calibrations proposed in the literature to derive $\log(N/O)$, together with those derived in this work. Columns: (1) Strong-line (SL) index or relevant strong-line ratios for that method. (2) Secondary parameter on which $\log(N/O)$ depends for that calibration. (3) Number and (4) nature of the objects used to derive the empirical calibration. (5) Range of validity for the calibration as stated by the different authors. (6) Reference. (7) Standard deviation. (8) Median values for the N/O residuals (i.e. difference between the SL method for our sample of H II regions, and those derived from the T_e -based method, $\log(N/O)_{SL} - \log(N/O)_{T_e}$). (9) Method used for the determination of $\log(N/O)$ for the calibrating targets in column (4): from the T_e -based method (T_e), PhM, R and C methods (R,C), and the H II-CHI-mistry (HCM) method.

Index or strong-line ratio(s) (1)	Secondary parameter (2)	N (3)	Calibration ^a objects (4)	Validity ^b range (dex) (5)	Ref. ^c (6)	Residuals stdev (dex) (7)	Median residuals (dex) (8)	Method (9)
N2O2		536	H II regions	$-1.74 < N2O2 < 0.62$	TW	0.08	0.002	T_e
N2O2	log(O/H)	536	H II regions	$-1.74 < N2O2 < 0.62$	TW	0.04	-0.004	T_e
N2O2		475	H II regions (MW, MC) (43), GEHRs (161), H II galaxies (271)	$-2.0 < N2O2 < 0.3$	PM09	0.13	0.21	T_e
N2O2		48	H II regions	$-1.45 < N2O2 < 0.15$	LS15	0.09	0.04	T_e^d
N2O2		414	H II regions (P12)	$-1.7 < N2O2 < 0.2$	ST17	0.09	0.05	T_e
N2O2		148	KBSS galaxies, $\langle z \rangle = 2.3$	$-1.7 < N2O2 < -0.2$	ST18	0.11	0.05	PhM
N2O2		27	LBAs ($z < 0.3$)	$-1.5 < N2O2 < -0.5$	LA20	0.09	0.02	T_e
N2O2		1240	EELGs ($\langle z \rangle = 0.08$)	$-1.7 < N2O2 < -0.5$	PM21	0.12	0.14	T_e
N2O2		118 478	SFGs (<i>stacks</i> , $\langle z \rangle = 0.072$)	$-1.25 < N2O2 < 0.1$	HP22	0.09	-0.06	T_e
N2S2		530	H II regions	$-0.58 < N2S2 < 0.84$	TW	0.19	-0.004	T_e
N2S2		475	H II regions (MW, MC) (43) GEHRs (161), H II galaxies (271)	$-1.4 < N2S2 < 1$	PM09	0.21	0.24	T_e
N2S2		148	KSBB galaxies, $\langle z \rangle = 2.3$	$-0.6 < N2S2 < 0.3$	ST18	0.19	0.07	PhM
N2S2		-	SFGs ($0.03 \leq z \leq 0.37$)	$-0.58 \leq N2S2 \leq -0.02$	A10	0.34	0.37	T_e
N2S2		1240	EELGs ($\langle z \rangle = 0.08$)	$-0.8 < N2S2 < 0.3$	PM21	0.19	0.06	T_e
N2S2		118 478	SFGs (<i>stacks</i> , $\langle z \rangle = 0.072$)	$-0.5 < N2S2 < 0.3$	HP22	0.20	0.16	T_e
O3N2		530	H II regions	$-1.61 < O3N2 < 2.86$	TW	0.15	0.03	T_e
O3N2	log(O ₃₂)	530	H II regions	$-1.61 < O3N2 < 2.86$	TW	0.09	0.03	T_e
N2		294	H II regions	$-1.5 < N2 < -0.65$	TW	0.13	0.01	T_e
N2	log(O ₃₂)	294	H II regions	$-1.5 < N2 < -0.65$	TW	0.09	-0.003	T_e
N2		148	KSBB galaxies, $\langle z \rangle = 2.3$	$-1.6 < N2 < -0.3$	ST18	0.15	-0.02	PhM
N ₂ , R ₂		313	H II regions	$-0.7 \leq \log(N2) \leq -0.45$	PG16	0.09	0.03	T_e (R,C)
N2O2, R ₂₃		38 478	SFGs ($0.04 \leq z \leq 0.25$)	$-1.8 \leq \log(N/O) \leq -0.1$	LI06	0.09	-0.03	PhM
[O II], [O III] [N II], [S II]		550	H II regions (MW, MC) GEHRs, H II galaxies	-	PM14	0.13	0.06	PhM (HCM)

Notes.

^aAcronyms as follow: EELGs (Extreme emission-line galaxies), GEHRs (Giant extragalactic H II regions), KBSS (Keck Baryonic Structure Survey), LBA (Lyman Break analogues), MC (Magellanic Cloud), MW (Milky Way), and SFGs (Star-forming galaxies).

^bValidity ranges are approximate and are deduced from the figures in the original papers, except in Pérez-Montero et al. (2021), Amorín et al. (2010), and Pilyugin & Grebel (2016), where they are given explicitly by the authors.

^cTW: This work; PM09: Pérez-Montero & Contini (2009); ST17: Strom et al. (2017); ST18: Strom et al. (2018); LA20: Loaiza-Agudelo et al. (2020); LS15: López-Sánchez et al. (2015); A10: Amorín et al. (2010); LI06: Liang et al. (2006); PM14: Pérez-Montero (2014b); PG16: Pilyugin & Grebel (2016); PM21: Pérez-Montero et al. (2021); HP22: Hayden-Pawson et al. (2022).

^dThe N/O abundances in LS15 were derived from an empirical determination of T_e , from their derived $12 + \log(O/H)$ abundances.

-0.3. The differences between their and our calibration might then be produced by their larger concentration of regions in the lowest abundance area (bottom-left part of the plot), with respect to our sample, in which the data are more uniformly distributed. In addition, it is important to note that the Pilyugin et al. (2012) sample is dominated by H II regions from irregular galaxies whose location in the $\log(N/O)$ -N2O2 diagram is slightly shifted towards higher N/O for a given N2O2 value, with respect to the average trend for the H II regions in spirals. Our more uniform distribution of values across the N2O2 axis, joined to the absence of H II regions from irregulars in our sample, might be the reason why we find it necessary a second order polynomial to properly fit the $\log(N/O)$ -N2O2 relation. We will further discuss this point in Section 5.

In addition to the empirical calibration of N2O2 based exclusively on H II regions, in Table 3 and Fig. 5 we compare our calibration with those by PM09, LA20, PM21, and HP22, respectively, based on other types of calibrating objects. PM09 use a sample of 271 H II galaxies, 161 giant extragalactic H II regions, and 43 H II regions of the Milky Way and Magellanic Clouds; 475 objects in total. The PM09 calibration clearly deviates from ours, being the offset greater than ~ 0.5 dex for the highest values of N2O2. The scatter in the $\log(N/O)$ -N2O2 plot of the calibration sample in PM09 is considerably high (see their fig. 10). This, together with their fitting method (a least-squares bisector linear fit) could explain, at least in part, the observed deviation from our best-fitting line.

The calibrations of the N2O2 index performed by LA20 and PM21 are also based on T_e -based N/O abundances, but on these cases

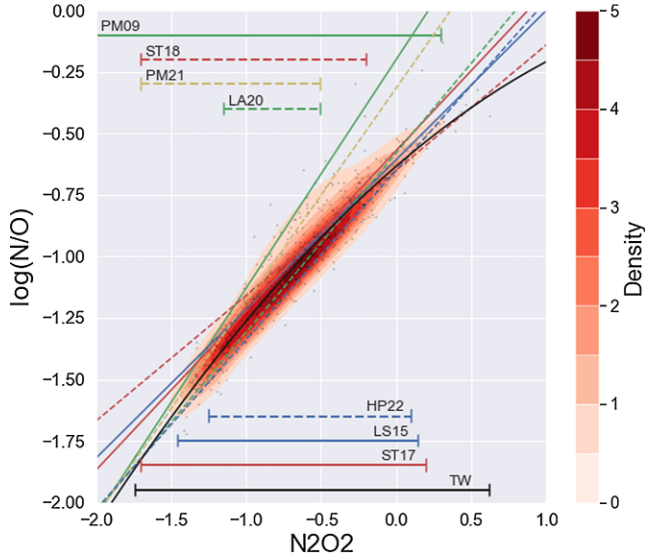


Figure 5. Direct-method N/O abundance versus strong-line ratio N2O2: Dots are individual values and red represents the density map. Fit from Equation (1) is shown in black continuous line (TW). Besides, we show other calibrations of N2O2 compiled from the literature: Pérez-Montero & Contini (2009; PM09), López-Sánchez et al. (2015; LS15), Strom et al. (2017; ST17), Strom et al. (2018; ST18), Loaiza-Agudelo et al. (2020; LA20), Pérez-Montero et al. (2021; PM21), and Hayden-Pawson et al. (2022; HP22).

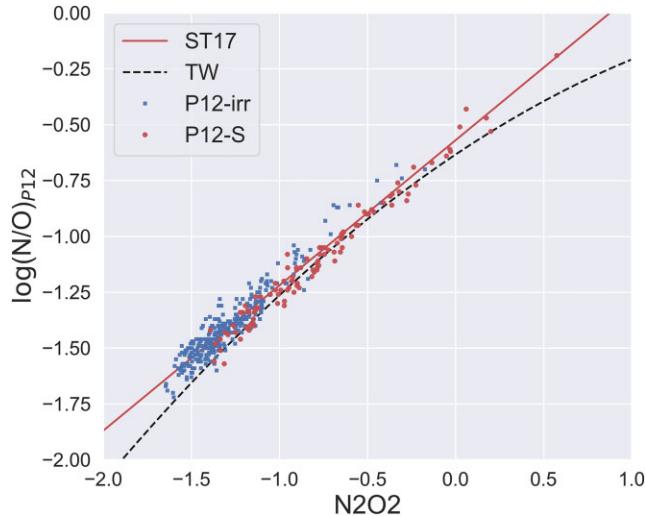


Figure 6. T_e -values for $\log(N/O)$ versus N2O2 index. Abundances are obtained by Pilyugin et al. (2012). Blue squares are H II regions in irregular galaxies and red dots correspond to H II regions belonging to spiral galaxies.

for samples of nearby galaxies, selected to be local analogues of higher redshift galaxies. Therefore, their calibrations are intended to be useful for abundance estimates for more distant galaxies. The calibrating sample of LA20 is composed by 27 galaxies with $z < 0.3$, but with properties similar to Lyman break galaxies (LBGs, i.e. luminous, compact, and having similar rest-frame far-UV properties to typical LBGs). The one used by PM21 is much larger, with 1240 extreme emission-line galaxies (EELGs), at redshifts $0.00 < z < 0.49$, extracted from the SDSS-DR7 (Sánchez Almeida et al. 2010). Both the LA20 and PM21 calibrations are derived from data within a similar N2O2 range (approximately from -1.7 to -0.5 , cf. from -1.7 to $+0.6$ in our calibration for only H II regions). However,

the LA20 and PM21 analytical calibrations of N2O2 have different slopes (Fig. 5), and this translates in an increasing difference in the $\log(N/O)$ values derived from them as the N2O2 index increases. Thus, $\log(N/O)$ as derived from PM21 is ~ 0.2 dex larger than the value derived from the LA20 calibration at the top end of their validity range ($N2O2 \sim -0.5$). The LA20 calibration is in rather good agreement with our derived ones (equations 1 and 2), in spite of the different nature of the calibrating targets. This is clearly visible in Fig. 5, but also in columns 7 and 8 in Table 3 that shows that this calibration, when applied to our H II region sample, yields some of the smallest values for the median residuals [difference between the T_e -based $\log(N/O)$ and the $\log(N/O)$ values derived from this calibration], 0.09 dex, and for the standard deviation (0.02 dex; cf. 0.14 and 0.12 dex for median residuals and standard deviation, respectively, for the PM21 calibration).

HP22 has recently derived an empirical calibration of N2O2 from integrated galaxy spectra. It is based on T_e -based N/O abundances for stacked Sloan Digital Sky Survey (SDSS) spectra of star-forming galaxies at redshift $0.07 < z < 0.25$ (Curti et al. 2017). It covers a smaller N2O2 range than ours, between -1.25 and 0.1 , and underestimates $\log(N/O)$ for most of the H II regions in our sample, as seen in the median residuals value, which is -0.06 dex, although with low standard deviation (0.09).

The ST18 calibration of N2O2 is also derived from integrated galaxy spectra, but relies on N/O abundances derived from PhM (Cloudy; Ferland et al. 2013). The calibration sample comprises 148 high-redshift galaxies ($\langle z \rangle = 2.3$) from the KBSS with index values in the range $-1.7 < N2O2 < -0.2$ dex. This calibration has its larger departure from ours at low values of N2O2, $-1.7 < N2O2 < -1.2$, but traces well the T_e -based $\log(N/O)$ -N2O2 relation for our sample of H II regions for $N2O2 \gtrsim -0.9$.

Finally, we would like to point out that, although not shown here for simplicity, we have carefully analysed the differences between the derived $\log(N/O)$ values for the N2O2 calibrations mentioned above, and the T_e -based estimates, in plots similar to the one shown in Fig. 2. These differences or residuals show a clear correlation with the $12 + \log(O/H)$ from the T_e -based method for all calibrations analysed in this section.

4.2 Methods based on the N2S2 and N2 indices

There are not many calibrations of these indices for the derivation of $\log(N/O)$, but the ones available are shown in Fig. 4. For the N2S2 index, PM09, ST18, PM21, and HP22 provide calibrations obtained from the samples and methods already described in Section 4.1. Amorín et al. (2010, hereinafter A10) also derive an empirical calibration of the N2S2 index from T_e -based abundances for a sample of star-forming galaxies selected from the SDSS. As for the calibration of N2O2 derived from galaxy integrated spectra, the N2S2 index range covered by these calibrating samples is smaller than the one covered by our H II region sample. The calibrations by ST18 and PM21 are the ones that better match the T_e -based abundances of our sample of H II regions, having similar slopes in the $\log(N/O)$ -N2S2 plane to ours, while the ones by PM09, A10, and HP22 have a steeper slope. The $\log(N/O)$ values obtained from the PM09 and A10 calibrations are, on average, larger than the T_e -based ones by ~ 0.24 – 0.31 dex, in the upper bound of their corresponding validity range. This offset is larger than the data standard deviation (~ 0.19 dex). The HP22 calibration is valid in a short range of N2S2 values, $-0.5 < N2S2 < 0.3$ (c.f. $-0.58 < N2S2 < 0.84$, for our calibrating H II region sample). Its larger slope implies a slight overestimation of the

log(N/O)-predicted values from this method, which is comparable to the standard deviation of the residuals.

ST18, in addition to N2O2 and N2S2, also provide an empirical calibration for N2 that matches very nicely our derived calibration for this index (Fig. 4) in the validity range in common for the two calibrations, in spite that it was obtained from high-redshift galaxies. To our knowledge there is no published empirical calibration of the O3N2 index for the derivation of log(N/O).

4.3 Other methods

There are other methods that permit to estimate log(N/O) from several strong-line ratios. This is the case for the R calibration and the HCM method by Pilyugin & Grebel (2016) and Pérez-Montero (2014b), respectively.

Pilyugin & Grebel (2016) performed an empirical calibration (the R calibration) after updating the sample of P12. It uses the strong-line ratios $R_2 = I_{[O\text{II}]}(\lambda 3727 + \lambda 3729)/I_{H\beta}$ and $N_2 = I_{[N\text{II}]}(\lambda 6548 + \lambda 6584)/I_{H\beta}$. Their calibrating sample is a selection of 313 H II regions (out of 965), chosen because of having O/H and N/O abundances, as derived from a strong-line method (C method; P12), that differ less than 0.1 dex from the T_e -based ones. The calibrating H II region sample belongs to nearby spiral and irregular galaxies, and yields a relation valid in the range $-0.7 \lesssim \log N_2 \lesssim -0.45$, which corresponds approximately to the same N2O2 interval of the calibration derived in this paper. If we apply the R calibration to our H II region sample, we obtain a standard deviation of 0.09 dex and a median value of 0.03 dex for the differences between the R-calibration log(N/O) values and those derived from the T_e -based method, which are very similar to what we get for empirical calibrations of N2O2 using only H II regions (see Table 3).

The HCM (Pérez-Montero 2014b), based on a Bayesian-like comparison between a certain set of emission lines and the predictions from a large grid of PhM, was applied to the same H II region sample used in this paper. The results are widely discussed in Z21a, and also shown in Table 3.⁵

Also based on a combination of PhM (from Thurston, Edmunds & Henry 1996) and strong-line ratios ($[N\text{II}]\lambda 6548, 6583/[O\text{II}]\lambda 3727$ and R23), Liang et al. (2006) performed a calibration based on 38 478 star-forming galaxies from SDSS. Median value and standard deviation of residuals are very similar to those found with the Pilyugin & Grebel (2016) method.

5 DISCUSSION

We have derived new empirical calibrations for the estimation of the N/O abundance ratio in local Galactic and extragalactic H II regions, that make use of the strong-line ratios N2O2, N2S2, N2, and O3N2, being the calibration of N2O2 the one that best reproduces the T_e -based estimate (equations 1 and 2).

A key issue for any *empirical* strong-line method is the potential effect of sample bias. This occurs when the calibration sample from which T_e -based abundances are derived is not representative of the entire sample (including targets without auroral line detections) for which strong-line abundances will be estimated. Kewley, Nicholls &

⁵It is important to note that in Zurita et al. (2021a), HCM version 3 was used, that uses POPSTAR synthesis evolutionary models (Mollá, García-Vargas & Bressan 2009). The HCM results may change for different assumed model, e.g. for BPASS v2.1 models (Eldridge et al. 2017), more appropriated for EELGs as discussed in PM21.

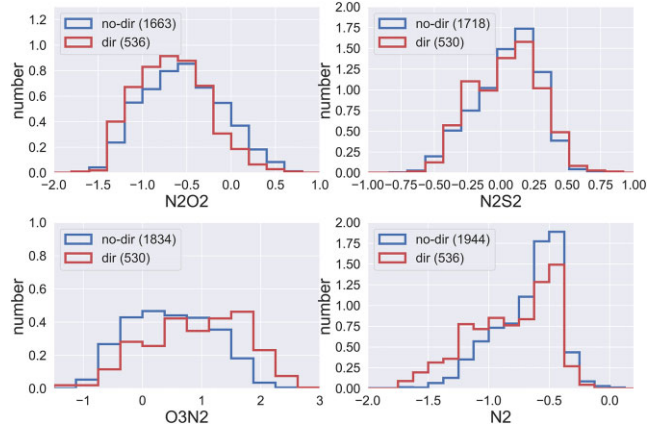


Figure 7. Normalized histograms showing the distribution of the indices used in this work (from left to right and from top to bottom N2O2, N2S2, O3N2, and N2) for the H II region calibration sample (in red) and the sample of H II regions without T_e -based N/O determinations (blue), both from Zurita et al. (2021a).

Table 4. Median index value and standard deviation (in dex) for the distributions of N2O2, N2S2, O3N2, and N2 for the sample of calibration H II regions (columns 2 and 3) and for the sample of H II regions without T_e -based N/O (columns 4 and 5).

Index	Calibration sample		Regions without <i>direct</i> N/O	
	Median value (dex)	stdev (dex)	Median value (dex)	stdev (dex)
(1)	(2)	(3)	(4)	(5)
N2O2	-0.67	0.40	-0.55	0.44
N2S2	0.06	0.25	0.08	0.25
O3N2	0.97	0.82	0.46	0.71
N2	-0.76	0.35	-0.61	0.27

Sutherland (2019) propose a simple exercise to test for sample bias, which is to compare the distribution of relevant emission-line ratios of the calibration sample (with T_e -based abundances) with that of the sample without T_e -based abundances. We show this comparison in Fig. 7 and Table 4 for the H II region collection used in this work (Z21a). Both the H II region calibration sample (in red) and the sample of regions without T_e -based N/O determinations (in blue) cover the same index ranges. The distributions for the two subsamples are very similar for all indices in terms of median values and standard deviations, specially for N2S2 and N2O2. The largest difference between the calibration sample and the sample of regions without T_e -based N/O occurs for O3N2, with the median value shifted ~ 0.5 dex towards larger values of O3N2, but this shift is not very relevant taking into account the width of the corresponding distributions (~ 0.8 dex).

The effect of sample bias is well illustrated by comparing our calibration sample with the one used by ST17. As already mentioned in Section 4.1, the N2O2 calibration of ST17 is the only one that exclusively uses extragalactic H II regions with T_e -based N/O abundances as calibrators (apart from ours and that of LS15 which is based on regions from a single galaxy). They use a large sample of H II regions from P12 in which most of them (309 out of 414) belong to irregular galaxies, rather than spirals as in our calibration.

In Fig. 8, we show the distributions of the N2O2, N2S2, O3N2, and N2 indices, for the P12 sample and, separately, for the subsamples of regions belonging to irregular (P12-Irr, in blue) or spiral (P12-

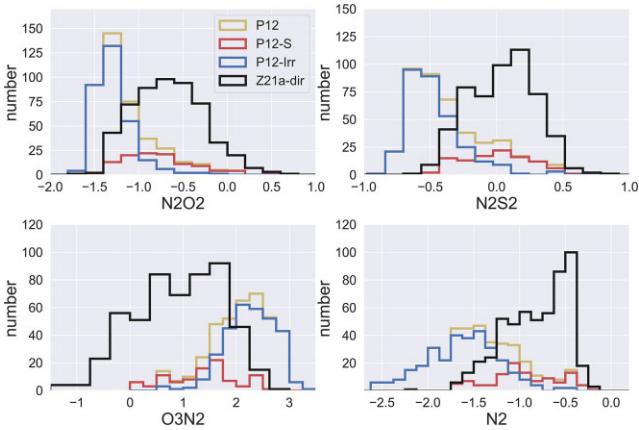


Figure 8. Distribution of the indices used in TW to estimate N/O values (from left to right and from top to bottom N2O2, N2S2, O3N2, and N2), considering several samples: H II regions with T_e -based N/O in Zurita et al. (2021a; Z21a-dir), H II regions with T_e -based abundances compiled by Pilyugin et al. (2012; P12). For the latter we also show the subsamples of H II regions belonging to spiral (P12-S) and irregular (P12-Irr) galaxies.

S, in red) galaxies in P12. We also show, for comparison, the distribution for our H II region calibration sample (Z21a-dir). It can be seen that the distributions for P12 (in yellow) and Z21a-dir (in black) are quite different, despite both being based on H II regions. However, ~ 75 per cent of the P12 H II region sample belong to irregular galaxies (P12-Irr), and these regions seem to be producing the differences in the index distributions between the P12 and Z21a-dir samples, as can be seen in the P12-Irr and P12-S comparison. But more important than the differences in the distributions themselves, is the fact that the two samples cover different ranges of index values, being especially evident for the O3N2 index, which covers much lower index values in Z21a-dir.

The differences in the distribution of N2O2 index values might then be the origin of the observed differences at high and low N/O values (Section 4.1) between the N2O2 calibration derived in TW and the one derived by ST17. This is easily seen in Fig. 6, where the T_e -based N/O for the ST17 calibration sample (P12) is plotted as a function of N2O2. The larger content of H II regions from irregulars in the P12 sample (blue squares in Fig. 6) and their concentration towards lower values of N2O2, yields a linear $\log(N/O)$ –N2O2 relation that differs from the second-order polynomial necessary to properly fit the data when the sample is exclusively based on H II regions in spirals (equation 1), with a more uniform sampling across the $\log(N/O)$ –N2O2 sequence. Therefore, the ST17 calibration, if applied to H II regions in spirals in their validity range ($-1.7 < N2O2 < 0.2$) would bias the derived strong-line N/O towards larger values for regions with low $\log(N/O)$ ($\lesssim -1.25$ dex) or N2O2 ($\lesssim -1.1$). The subsamples P12-Irr and P12-S are also plotted in the $\log(N/O)$ versus N2S2, O3N2, and N2 diagrams in Fig. 9. The H II regions from irregulars also produce a bias in them, but the higher dispersion in these relations dilutes their effect.

The differences observed between our and other previous strong-line calibrations of N2O2 to derive N/O, are more difficult to interpret when the calibrating samples are different from H II regions and/or their abundances are obtained from PhM rather than T_e -based determinations. In the lowest N/O range, the calibration of N2O2 with the largest difference with ours is the one derived by ST18, whose calibrators are high-redshift galaxies ($\langle z \rangle = 2.3$) with N/O abundances derived from PhM. However, their derived $\log(N/O)$ –

N2O2 relation shows a reasonably good overlapping with our sample of local H II regions in the range $-1 < N2O2 < -0.5$, where ST18 have the bulk of their data and these have the lowest scatter (see their fig. 11). The calibration derived by LA20 for nearby analogues of LBGs is also in good agreement with ours in their range of validity. The same is not true for the one obtained by PM21 for EELGs, which has a steeper slope than ours and those of ST18 and LA20. There is an issue that may be relevant to explain the differences between TW and those cited above. Although the redshift range of the PM21 ($0 < z < 0.49$) sample overlaps with that of LA20 ($z < 0.3$), the PM21 sample has an average redshift of 0.08 with only 10 per cent of the galaxies in their sample having $z > 0.194$. The 3 arcsec of the SDSS fibre includes flux from the central region of the sample galaxies in PM21 (~ 5 kpc for their average redshift, z). The abundances of ST18 and LA20 come, however, from integrated fluxes from the whole disc. More difficult is the comparison with HP22. They consider low-redshift galaxies ($z < 0.25$, $\langle z \rangle = 0.072$) and use SDSS spectra, with the fibre including only the emission from the central part of the galaxies, as in PM21, but in this case the emission-line fluxes have been estimated for stacked SDSS spectra.

The $\log(N/O)$ –N2S2 relation has a larger scatter than the one for the N2O2 index, but it is very useful, given the proximity in the spectra of the involved emission lines. There are five calibrations of this index from previous work (shown in Table 3 and Fig. 4). As with the N2O2 calibration, the one obtained by ST18, despite being obtained with integrated spectra of galaxies at $\langle z \rangle = 2.3$, is in good agreement with ours, while those of A10, HP22, and PM09, obtained from more nearby galaxies (as well as H II regions, in the case of PM09), show a steeper slope. These similarities in the calibration obtained from H II regions of local galaxies and high-redshift galaxies were already found by ST18, who pointed out to similarities between the nebular spectra of H II regions and integrated spectra of high-redshift galaxies as the cause, perhaps because the latter are dominated by one or several dominant H II regions, as opposed to closer galaxies, where SF is more distributed in the discs (e.g. Sanders et al. 2016; Kashino et al. 2017; LA20). However, there are well-known differences between the spectral properties of H II regions and those of high-redshift galaxies (or their local analogues), namely their different location in the $[O III]\lambda 5007/H\beta$ versus $[N II]\lambda 6584/H\alpha$ BPT (Baldwin et al. 1981) diagram (e.g. Steidel et al. 2014; Steidel et al. 2016; ST17, ST18; Sanders et al. 2021).

As commented before regarding the differences with the PM21 for N2O2, calibrations obtained with nearby galaxies are also usually based on SDSS spectra, which do not include the integrated emission of the whole galaxy, but of the central area, which, depending on its extent and on the galaxy properties, may be more or less representative of the integrated spectrum of the galaxy. The different covering fraction of the galaxy light in integrated spectra of galaxies may cause part of the observed differences between different calibrations (e.g. Kewley, Jansen & Geller 2005; Liang et al. 2006). However, this argument does not explain the reasonably good agreement of our calibration with the one from PM21 for N2S2, which includes only a part of the light emitted by the galaxies, given the mean redshift ($\langle z \rangle = 0.08$) of their sample.

With respect to integrated spectra, an additional aspect, which may be of great relevance to the abundances of the ionized gas, among others, is the possible inclusion of emission from the diffuse ionized gas (DIG, e.g. Zurita, Rozas & Beckman 2000; Oey et al. 2007) in spectra that integrate emission from all or part of the galaxy (see e.g. Sanders et al. 2017; Zhang et al. 2017; Vale Asari et al. 2019), as the emission-line ratios in this low surface brightness component

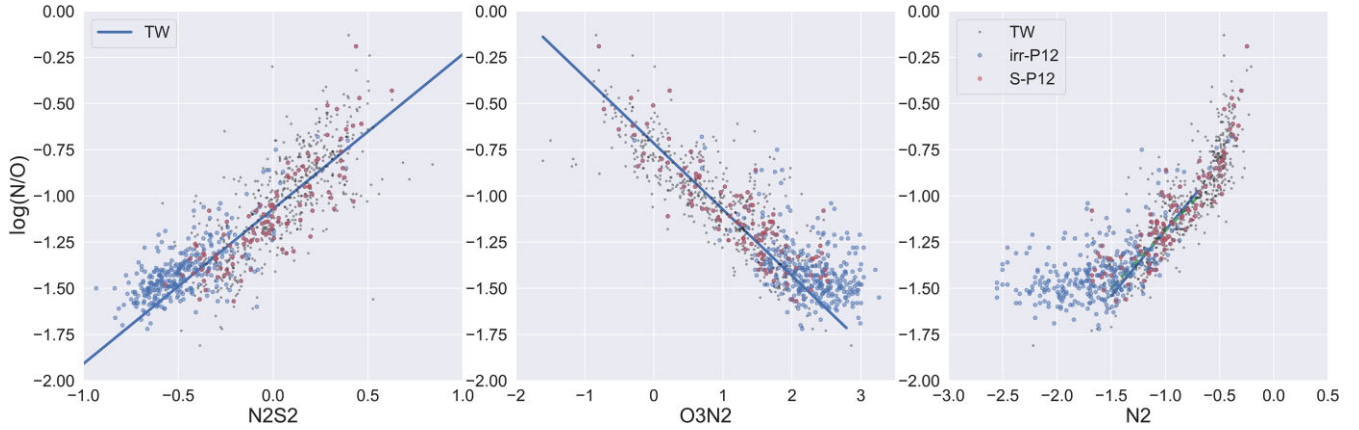


Figure 9. The same as Fig. 4 but showing the sample of H II regions with T_e -based abundances from P12 with blue or red dots depending on whether they are located in irregular or spiral galaxies, respectively.

differ from those measured in classical H II regions. The DIG could therefore differentially affect the indices used to trace abundances when these are derived from integrated spectra that includes both H II region and DIG emission. The $[\text{S II}]/\text{H}\alpha$ emission is enhanced in the DIG (more than that of $[\text{N II}]/\text{H}\alpha$ ratio)⁶ with respect to the H II regions (e.g. Domgorgen & Mathis 1994; Galarza, Walterbos & Braun 1999). Therefore, in the integrated spectra of galaxies, we would expect a lower N2S2 for a given N2O2 than for individual H II regions.

Fig. 10 shows (as a density map) the ratio of the N2S2 and N2O2 indices for our sample of H II regions in local spirals (Z21a) and, for comparison, the relations between these two indices derived by previous authors: namely, the relation derived by ST18 for high-redshift galaxies (ST18-KBSS), those derived by the same authors for nearby galaxies from SDSS spectra (ST18-SDSS), and for the P12 H II region sample (in local spirals and irregulars) and the relation derived by PM09, including H II galaxies and H II regions. It is clearly seen that for a given N2O2, the N2S2 relation derived from the integrated spectrum of local galaxies (ST18-SDSS) is lower by ~ 0.2 – 0.25 dex. This is expected in the case of contamination of DIG emission in the spectra. However, this does not seem to affect the integrated spectra of high-redshift galaxies. A possible explanation is a decreasing contribution of the DIG component with increasing redshift. As discussed by Sanders et al. (2017), high-redshift galaxies have both a smaller size and a higher SFR, at a fixed M_* , than their low-redshift analogues. Therefore, they have both a higher specific SFR and $\text{H}\alpha$ surface brightness. The mean DIG emission fraction decreases with increasing $\text{H}\alpha$ surface brightness of galaxies (Oey et al. 2007). The agreement in the N2S2–N2O2 ratio for resolved H II regions and integrated outflows of high-redshift galaxies could be due to a much smaller impact of the DIG on the integrated fluxes of these galaxies. Finally, we observe again in Fig. 10 the different location and trend of the H II regions of irregular galaxies, which explains the steeper slope of the N2S2–N2O2 relation obtained by ST17.

There are a number of additional methods to derive N/O, that make use of a combination of the same or other ratios of strong emission lines (bottom rows in Table 3), namely the ones by Liang et al. (2006), Pérez-Montero (2014b), and that from Pilyugin &

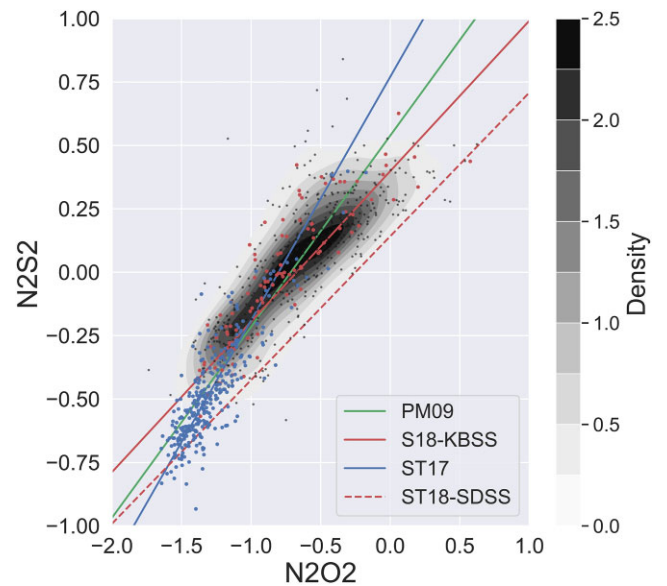


Figure 10. N2S2 versus N2O2 for the calibration sample from the H II region calibration sample used in this work (Z21a), represented as a grey-scale density map and with black dots. We also show the best linear fits derived by other authors for different data samples: those of ST18 for Keck Baryonic Structure Survey (KBSS) galaxies at $\langle z \rangle \sim 2$, and for local SDSS galaxies (red solid and dashed lines, respectively); that of PM09 for H II galaxies and H II regions (green line), and the relation derived by ST17 for the H II regions sample of P12 (blue solid line). The H II regions of the P12 are also shown with blue or red dots depending on whether they belong to irregular or spirals galaxies, respectively.

Grebel (2016). We have applied these methods to our H II region calibration sample and they give a good overall prediction of the T_e -based N/O abundances, with low values for the median and standard deviation for the differences between the strong-line and the T_e -based abundances for all the regions. However, it should be noted that the results obtained with the analytical calibration of the N2O2 index derived in this work give similar or even better results than these methods, with the added advantage of being straightforward to apply.

A final issue that it is worth mentioning here regards the N/O–O/H relation. Some calibrations rely in a assumed relation between $\log(\text{N/O})$ and $\log(\text{O/H})$ (see e.g. Dopita et al. 2016).

⁶In fact, the N2O2 is the least sensitive strong-line diagnostic to the DIG and active galactic nucleus emission (Kewley et al. 2006; Zhang et al. 2017).

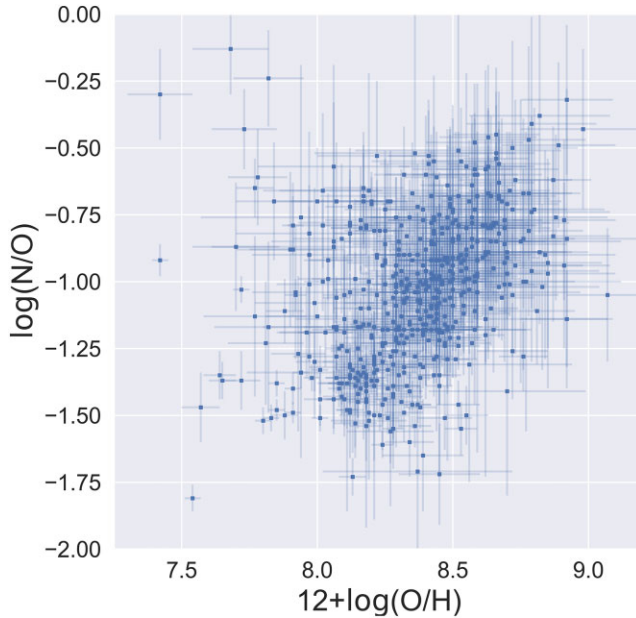


Figure 11. $\log(N/O)$ versus $12 + \log(O/H)$ for our H II region calibration sample or regions with T_e -based N/O and O/H abundances in Z21a. The median error values are: 0.17 dex for $\log(N/O)$ and 0.1 dex for $12 + \log(O/H)$.

The indices used in this paper as tracers of the N/O abundance ratio in H II regions, are also used as metallicity tracers (see Section 3 and references therein). A tight relation in the $\log(N/O)$ – $\log(O/H)$ relation would easily explain their usefulness for the two abundance ratios. However the $\log(N/O)$ – $\log(O/H)$, in Fig. 11, for our sample of H II regions with T_e -based abundances, has a large dispersion $\gtrsim 0.26$ dex, three times larger than the dispersion in the $\log(N/O)$ –N2O2 relation for the same sample of H II regions (see Table 2). This fact strengthens the goodness of our N2O2 calibration, which is not determined by a tight N/O–O/H relation.

6 CONCLUSIONS

We have used a large sample of 536 H II regions in nearby spiral galaxies with T_e -based (*direct*) abundances to test the usefulness of some of the most frequently used strong-line ratios that involve the $[N\text{II}]\lambda 6583$ emission-line flux as tracers of the N/O abundance ratio in H II regions. The calibration H II region sample is extracted from the compilation performed by Z21a, for which T_e -based abundances were calculated from the compiled emission-line fluxes with a homogeneous methodology. The four indices analysed (N2O2, N2S2, O3N2, and N2) are strongly correlated with the T_e -based $\log(N/O)$, with Spearman’s rank correlation coefficients larger than 0.8 [c.f. ~ 0.6 with $12 + \log(O/H)$]. The strongest correlation is found for the N2O2 index ($\rho = 0.95$), with the best-fitting function for the $\log(N/O)$ –N2O2 relation being a second-order polynomial:

$$\log(N/O)_{\text{N2O2}} = (-0.102 \pm 0.018) \times \text{N2O2}^2 + (0.528 \pm 0.019) \times \text{N2O2} - (0.634 \pm 0.006). \quad (3)$$

This relation is valid in the range of $-1.74 < \text{N2O2} < 0.62$, which implies a wide range of ~ 1.1 dex in $\log(N/O)$, with low dispersion in the fitting residuals (rms ~ 0.09). These show a positive correlation with the T_e -based oxygen abundance that, if taken into account in

the fitting (equation 2 and Table 2), reduces the dispersion down to ~ 0.04 dex.

The dependence of the T_e -based $\log(N/O)$ on the other three indices (N2S2, O3N2, and N2) fits well with a single linear fit, but the dispersion of the residuals is larger (rms ~ 0.13 – 0.20 dex) than for N2O2, and their range of validity smaller, especially for N2 that saturates for high values of N2 ($\gtrsim -0.65$). These results, joined to its virtually independence on the ionization parameter, make N2O2 the preferred index for deriving $\log(N/O)$ in H II regions when the electron temperature is not available.

Although these relations have been derived for H II regions in local galaxies, there is good agreement between our calibrations and the ones derived for integrated fluxes of high-redshift galaxies by previous authors (e.g. ST18 and LA20, in the range of validity in common). The N2O2 index is also one of the indices less altered by contamination from the DIG emission (e.g. Zhang et al. 2017) and it is virtually independent of the ionization parameter (e.g. Dopita et al. 2000). These properties of the N2O2 index, joined to the observed agreement between our calibration of the N2O2 and previous calibrations of this index for the integrated emission of high-redshift galaxies in the common validity range, make the N2O2 calibration derived in this paper tentatively promising for N/O estimates for integrated fluxes of high-redshift galaxies. Caution is however mandatory until proper calibrations based on sufficient T_e -based N/O abundances for high-redshift galaxies (or analogues) become available.

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DATA AVAILABILITY

The data underlying this article are available in the article and are based on a compilation performed by Zurita et al. (2021a) that is publicly available on the CDS VizieR facility (via <https://vizier.u-strasbg.fr/viz-bin/VizieR>).

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