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

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ABSTRACT

We use a sample of 536 H II regions located in nearby spirals, with an 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 $-1.81 < \log(\text{N/O}) < -0.13$). 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 – HII regions – galaxies: spiral – galaxies: ISM – galaxies: abundances

1 INTRODUCTION

Most of the chemical elements heavier than hydrogen and helium are produced 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 et al. 1980; Bresolin et al. 2004; Kewley et al. 2010; Pilyugin et al. 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 timescale via the explosion of type II SNe, 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. Vincenzo et al. 2016; Edmunds & Pagel 1978; Gavilán et al. 2006). It is produced from C and O through the CNO cycle for the combustion of H in He, being most of it (~ 74\%) produced in low- and intermediate-mass stars (LIM stars, $\lesssim 8M_\odot$), according to chemical evolution models (e.g. Matteucci 1986; Chiappini et al. 2003; Kobayashi et al. 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 star formation history of the galaxy or the H II region (e.g. Vincenzo et al. 2016; Mollá et al. 2006; Köppen & Hensler 2005). 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 et al. 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. Andrews & Martini 2013; Amorín et al. 2010; Vincenzo et al. 2016; Loyaiza-Agudeño et al. 2020; Luo et al. 2020). 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. Maiolino & Mannucci 2019; Vangioni et al. 2018; Pérez-Montero et al. 2021, 2013; Sanders et al. 2018; Masters et al. 2014).

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. (2021) find the same anti-correlation of N/O with SFR as O/H. Hayden-Pawson et al. (2021) 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 vs. N2O2, Hayden-Pawson et al. 2021).

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 ($[\text{O} \text{iii}]/\lambda6300,3729$ and $[\text{N} \text{ii}]/\lambda6583$) 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; Arellano-Córdova & Rodríguez 2020; Esteban & García-Rojas 2018).

Although it is not without problems (e.g. Stasińska 2002; Bresolin 1996), the so-called direct or $T_e$-based method$^1$ (e.g. Bresolin et al. 2004; Berg et al. 2020; Pérez-Montero 2014a) 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 10m class telescopes (Bresolin 1996). An alternative method is that based on measurements of optical metal recombination lines, where the ionic 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. Esteban et al. 2020; Toribio San Cipriano et al. 2016; García-Rojas et al. 2006).

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 (e.g. Gaugh 1991; Kewley & Dopita 2002; Dopita et al. 2016). Both photoionization models and methods based on metal recombination lines tend to estimate larger oxygen abundances than the $T_e$ method (e.g. Bresolin et al. 2009; Zurita et al. 2021a; Esteban et al. 2018) 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. Dopita et al. 2016; Brown 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 are 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 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 organised as follows. In Section 2 we summarise 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 HII 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 regions$^2$ from 51 nearby ($< 64$ Mpc) spiral galaxies with absolute B-band magnitudes between -22 and -17, and inclinations lower than 70$^3$.

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 methodology$^3$. The direct abundances range from 7.42 to 9.07 for 12+log(O/H), and from -1.81 to -0.13 for log(N/O).

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

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

$^2$ Some 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.

$^3$ The 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 of emission-line flux measurements (see Section 3.1 in Zurita et al. 2021a).
gas-phase of star-forming galaxies, and (2) to derive new empirical strong-line methods for the derivation of N/O in H\textsc{ii} regions. Our calibrating sample comprises the 536 H\textsc{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\textsc{ii} regions within spiral galaxies alone, in contrast with previous samples that included H\textsc{ii} regions from different galaxy types and/or integrated fluxes from galaxies (e.g. Pérez-Montero & Contini 2009; Pilyugin et al. 2012; Liang et al. 2006).

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\textsc{i}], 6583, [O\textsc{ii}], 5007, [O\textsc{iii}], 3727 and/or [S\textsc{ii}], 6717, 6731 emission lines, besides the H\textalpha and H\beta 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,...). In particular, those including the [N\textsc{i}], 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\textsc{i}], 6583 emission-line flux:

- $N_2 = \log([N\textsc{i}],6583/H\alpha)$
- $O3N2 = \log([O\textsc{iii}],5007/H\beta/[N\textsc{i}],6583/H\alpha)$
- $N2O2 = \log([N\textsc{i}],6583/[O\textsc{ii}],3727)$
- $N2S2 = \log([N\textsc{i}],6583/[S\textsc{ii}],6717,6731)$

The $N_2$, O3N2 and N2O2 indices are widely used for the derivation of O/H (see e.g. Shapley et al. 2005; Sánchez-Menguiano et al. 2018; Ho et al. 2015, respectively). The $N_2$ index (Storchi-Bergmann et al. 1994; Denicolo et al. 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 et al. 1981a), 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 Allin 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\textsc{ii} region ionization parameter (e.g. Ho et al. 2015; Zurita et al. 2021a) and it saturates at low oxygen abundances (12+log(O/H) $\lesssim$ 8, Pérez-Montero & Contini 2009).

The N2S2 index also makes use of close-by in wavelength emission lines, but it considers the [S\textsc{ii}], 6717, 6731 doublet, which is fainter and therefore more difficult to detect. It was first proposed as a metallicity indicator for H\textsc{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\textsc{ii} regions with 12+log(O/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 et al. 2006; Zurita et al. 2021a).

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

| Index   | N   | $\rho$ | $N$ | $\rho$ |
|---------|-----|-------|-----|-------|
| 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 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-Córduva et al. 2020; Zurita et al. 2021a).

We have used our sample of H\textsc{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 ($\rho$) between the H\textsc{ii} region values for each index, and the corresponding $T_e$-based log(N/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(N/O), with values of $\rho$ 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(O/H) is lower than for log(N/O), indicating moderate correlations, with $\rho$ 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(N/O) for our H\textsc{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(N/O) abundance ratio derived from the $T_e$-method against the N2O2 index. Individual H\textsc{ii} region values are indicated with black dots. An underlying density map for the same data set is shown in red colors, that allows a better inspection of the distribution in areas of the plot with a high overlapping of data-points (darker red).

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 to the data is obtained with a second-order polynomial, with weights equal to the reciprocal of the squared uncertainties in log(N/O) and yields

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

(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_3N2)/([O I]λ4959, 5007)/([O II]λ3727)) as a proxy for the ionization parameter in the H II regions. It can be clearly seen that the residuals from our fit (Eq. 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 logO_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:

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

(2)

The fitting residuals from Eq. 2 are shown in the bottom panels of Fig. 2. There are no significant dependences 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 Eq. 2 from 0.085 to 0.041 dex. Their median value is however slightly higher now than with the fitting from Eq. 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-fittings (Eq. 1 and Eq. 2) as a function of the N2O2 parameter with yellow triangles and black dots, respectively. It is important to note that although Eq. 2 yields a better fitting to the data, the empirical calibration of N2O2 to derive log(N/O) given in Eq. 1 is already very good. Eq. 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 [Ni II]λ6583 emission line. Even though, for these objects, Eq. 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 Eq. 1 and Eq. 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 (ρ ~ 0.78 ~ 0.88) and, in any case, much stronger than their correlation with 12 + log(O/H), with ρ ~ 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. López-Sánchez et al. 2011; Marino et al. 2013; Pérez-Montero & Contini 2009; Pérez-Montero & Díaz 2005, and references therein). In fact, we have seen this dependence for the residuals of the best-fittings 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. 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≥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 dependences on 12 + log(O/H), for N2O2, and 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.
New calibrations for estimating the N/O ratio

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\( \alpha \) 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\( \alpha \) region sample.

Except for the calibration performed by Strom et al. (2018) and López-Sánchez et al. (2015), hereinafter ST18 and LS15, respectively, all the rest have been obtained empirically from determinations 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 Strom et al. (2017), hereinafter ST17, are the only ones based exclusively on H\( \alpha \) regions. The calibration by LS15 is obtained from N/O abundances derived from an empirical determination of the \( T_e \) for 48 H\( \alpha \) regions of the galaxy pair NGC1510/NGC1512, with N2O2 values in the...
Figure 4. $T_e$-based log(N/O) abundance ratio vs. the strong-line ratios N2S2, O3N2 and N2. The blue straight line shows the 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. (2021) 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 color. 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.

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; (3) resulting empirical calibration; (4) validity range for the calibration given in column (3); (5) Spearman’s rank correlation coefficient between log(N/O) and the strong-line index in column (1), $x_1$, in this index range; (6) standard deviation and (7) median value of the fitting residuals, and (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) | $\rho$ | Residuals (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(O32) | $(-0.73 \pm 0.01)x_1 - (0.29 \pm 0.02) + (0.74 \pm 0.02)x_2$ | $-1.61 < x_1 < 2.86$ | -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(O32) | $(0.85 \pm 0.03)x_1 - (0.40 \pm 0.03) + (0.33 \pm 0.02)x_2$ | $-1.5 < x_1 < -0.65$ | 0.74 | 0.09 | -0.003 | 294 |

range -1.45 – 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 (Eq. 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 galaxies and the rest are from irregular galaxies. As we can see in Fig. 5, the ST17 calibration almost matches the one performed in this work (Eq. 1) in the range -0.8 ≤ N2O2 ≤ -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 -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

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4 All 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.
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 Pérez-Montero & Contini (2009), Loyaiz-Agudelo et al. (2020), Pérez-Montero et al. (2021), and Hayden-Pawson et al. (2021), hereinafter PM09, LA20, PM21, and HP21, 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.

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 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 EELGs (Extreme Emission Line Galaxies), 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 ~ 0.5). The LA20 calibration is in rather good agreement with our derived ones (Eqs. 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).

HP21 has recently derived an empirical calibration of N2O2 from integrated galaxy spectra. It is based on T_e-based N/O abundances for stacked 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 residual 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 photoionization models (Cloudy, Ferland et al. 2013). The calibration sample comprises 148 high redshift galaxies (< z >= 2.3) from the Keck Baryonic Structure Survey (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 ~ 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 HP21 provide calibrations obtained from the samples and methods already described in subsection 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 HP21 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

Figure 5. Direct-method N/O abundance vs. strong-line ratio N2O2: dots are individual values and in red is represented the density map. Fit from Eq. 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), Loyaiz-Agudelo et al. (2020) (LA20), Pérez-Montero et al. (2021) (PM21) and Hayden-Pawson et al. (2021) (HP21).
Figure 6. $T_\epsilon$-values for log(N/O) vs. 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.

dex). The HP21 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, that 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 H ii-CHI-mistrty (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 Pilyugin et al. (2012). It uses the strong-line ratios $R_2 = I_{[OII]}(\lambda 3727 + \lambda 3729)/I_{H\beta}$ and $N_2 = I_{[NI]}(\lambda 6548 + \lambda 6584)/I_{H\beta}$. Their calibrating sample is a selection of 313 H ii region sample (out of 965), chosen because of having O/H and N/O abundances, as derived from a strong line method (C method, Pilyugin et al. 2012), that differ less than 0.1 dex from the $T_\epsilon$-based ones. The calibrating H ii region sample belongs to nearby spiral and irregular galaxies, and yields a relation valid in the range $-0.7 \leq \log N_2 \leq -0.45$, 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 $T_\epsilon$-based method, which are very similar to what we get for empirical calibrations of N2O2 using only H ii regions (see Table 3).

The H ii-CHI-mistry method (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 photoionization models was applied to the same H ii sample used in this paper. The results are widely discussed in Zurita et al. (2021a), and also shown in Table 5.

Also based on a combination of photoionization models (from Thurston et al. 1996) and strong-line ratios ([N ii]4649,6583/Hα) and R23), Liang et al. (2006) performed a calibration based on 38478 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 $T_\epsilon$-based estimate (Eqs. 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 $T_\epsilon$-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 et al. (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 $T_\epsilon$-based abundances) with that of the sample without $T_\epsilon$-based abundances. We show this comparison in Fig. 7 and Table 4 for the H ii region collection used in this work (Zurita et al. 2021a).

Both the H ii region calibration sample (in red) and the sample of regions without $T_\epsilon$-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 $T_\epsilon$-based N/O occurs for O3N2, with the median value shifted $\sim 0.5$ dex towards larger values of O3N2, but this shift is not very relevant taking into account the width of the corresponding distributions ($\sim 0.8$ 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 $T_\epsilon$-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 Pilyugin et al. (2012, P12 hereinafter) 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-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, $\sim 75$ 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

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5 It is important to note that in Zurita et al. (2021a), HCM version 3 was used, that uses POPSTAR synthesis evolutionary models (Mollá et al. 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.
New calibrations for estimating the N/O ratio

Table 3. List of strong-line calibrations proposed in the literature to derive log(N/O), together with those derived in this work (TW). Columns: (1) Strong-line 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 and (8) median values for the N/O residuals (i.e. difference between the SL method for our sample of H\textsc{ii} regions, and those derived from the T_e-based method, log(N/O))\textsubscript{SL} - log(N/O)\textsubscript{T_e}) and (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), photoionization models (PhM), R and C-methods (R,C) and the H T_e-CHI-mistry (HCM) method.

| Index or strong-line ratio(s) | Secondary parameter | N | Calibration\(^a\) \(\text{objects}\) | Validity\(^b\) range (dex) | Ref.\(^c\) | Residuals stdev (dex) | Median residuals (dex) | Method |
|-------------------------------|---------------------|---|-----------------------------------|---------------------------|-----------|----------------------|------------------------|--------|
| N2O2                          | log(O/H)            | 536 | H\textsc{ii} regions             | -1.74 < N2O2 < 0.62       | TW        | 0.08                 | 0.002                  | T_e    |
| N2O2                          | log(O/H)            | 536 | H\textsc{ii} regions             | -1.74 < N2O2 < 0.62       | TW        | 0.04                 | -0.004                 | T_e    |
| N2O2                          | H\textsc{ii} regions (MW, MC) (43), GEHRs (161), H\textsc{ii} galaxies (271) | 475 | –                               | -2.0 < N2O2 < 0.3         | PM09      | 0.13                 | 0.21                   | T_e    |
| N2O2                          | H\textsc{ii} regions | 48  | –                                | -1.45 < N2O2 < 0.15       | LS15      | 0.09                 | 0.04                   | T_e\(^d\) |
| N2O2                          | H\textsc{ii} regions (P12) | 414 | –                                | -1.7 < N2O2 < 0.2         | ST17      | 0.09                 | 0.05                   | T_e    |
| N2O2                          | KBSS galaxies, \(<22=2.3\) | 148 | –                                | -1.7 < N2O2 < -0.2        | ST18      | 0.11                 | 0.05                   | PhM    |
| N2O2                          | LBAs (\(z < 0.3\))  | 27  | –                                | -1.5 < N2O2 < -0.5        | LA20      | 0.09                 | 0.02                   | T_e    |
| N2O2                          | EELGs (\(<z>0.08\)) | 1240| –                                | -1.7 < N2O2 < -0.5        | PM21      | 0.12                 | 0.14                   | T_e    |
| N2O2                          | SFGs (\(<z>0.072\)) | 118478| –                              | -1.25 < N2O2 < 0.1        | HP21      | 0.09                 | -0.06                  | T_e    |
| N2S2                          | H\textsc{ii} regions | 530 | –                                | -0.58 < N2S2 < 0.84       | TW        | 0.19                 | -0.004                 | T_e    |
| N2S2                          | H\textsc{ii} regions (MW, MC) (43), GEHRs (161), H\textsc{ii} galaxies (271) | 475 | –                              | -1.4 < N2S2 < 1          | PM09      | 0.21                 | 0.24                   | T_e    |
| N2S2                          | KSBB galaxies, \(<22=2.3\) | 148 | –                                | -0.6 < N2S2 < 0.3        | ST18      | 0.19                 | 0.07                   | PhM    |
| N2S2                          | SFGs (\(0.03 < z < 0.37\)) | 148 | –                                | -0.58 < N2S2 < -0.02     | A10       | 0.34                 | 0.37                   | T_e    |
| N2S2                          | EELGs (\(<z>0.08\)) | 1240| –                                | -0.8 < N2S2 < 0.3        | PM21      | 0.19                 | 0.06                   | T_e    |
| N2S2                          | SFGs (\(<z>0.072\)) | 118478| –                              | -0.5 < N2S2 < 0.3        | HP21      | 0.20                 | 0.16                   | T_e    |
| O3N2                          | H\textsc{ii} regions | 530 | –                                | -1.61 < O3N2 < 2.86      | TW        | 0.15                 | 0.03                   | T_e    |
| O3N2                          | H\textsc{ii} regions | 530 | –                                | -1.61 < O3N2 < 2.86      | TW        | 0.09                 | 0.03                   | T_e    |
| N2                            | log(O_32)           | 294 | H\textsc{ii} regions             | -1.5 < N2 < -0.65        | TW        | 0.13                 | 0.01                   | T_e    |
| N2                            | log(O_32)           | 294 | H\textsc{ii} regions             | -1.5 < N2 < -0.65        | TW        | 0.09                 | -0.003                  | T_e    |
| N2                            | KSBB galaxies, \(<22=2.3\) | 148 | –                                | -1.6 < N2 < -0.3         | ST18      | 0.15                 | -0.02                  | PhM    |
| N2, R_2                       | log(N/2)            | 313 | H\textsc{ii} regions             | -0.7 < log(N2) < -0.45   | PG16      | 0.09                 | 0.03                   | T_e (R,C) |
| N2O2, R_23                    | SFGs (\(0.04 < z < 0.25\)) | 38478| –                                | -1.8 < log(N/O) < -0.1   | LI06      | 0.09                 | -0.03                  | PhM    |
| [O I]/[O III]                  | H\textsc{ii} regions (MW, MC), GEHRs, H\textsc{ii} galaxies | 550 | –                                 | –                         | PM14      | 0.13                 | 0.06                   | PhM (HCM) |

\(^a\) Acronyms as follows: EELGs (Extreme Emission-Line Galaxies), GEHRs (Giant Extragalactic H\textsc{ii} Regions), KBSS (Keck Baryonic Structure Survey), LBA (Lyman Break analogs), MC (Magellanic Cloud), MW (Milky Way), and SFGs (Star Forming Galaxies).

\(^b\) Validity 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.

\(^c\) TW: 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), HP21: Hayden-Pawson et al. (2021).

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

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\textsc{ii} regions (columns 2 and 3) and for the sample of H\textsc{ii} regions without T_e-based N/O (columns 4 and 5).

| Index | Median value (dex) | stdev (dex) | Median value (dex) | stdev (dex) |
|-------|-------------------|-------------|-------------------|-------------|
| 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        |

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 this work 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\textsc{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\textsc{ii} regions in spi-
N/O abundances derived from photoionization models. 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 analogs of Lyman Break Galaxies 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 a issue that may be relevant to explain the differences between this work 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% of the galaxies in their sample having z>0.194. The 3σ of the SDSS fibre includes flux from the central region of the sample galaxies in PM21 (~5 kpc for their average z). The abundances of ST18 and LA20 come, however, from integrated fluxes from the whole disc. More difficult is the comparison with HP21. Like PM21 they consider low redshift galaxies (z <0.25, <z>=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 has 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 <z>=2.3, is in good agreement with ours, while those of A10, HP21 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-z galaxies was already found by ST18, who pointed out to similarities between the nebular spectra of H ii regions and integrated spectra of high-z galaxies as the cause, perhaps because the latter are dominated by one or several dominant H ii regions, as opposed to closer galaxies, where star formation is more distributed in the discs (e.g. Sanders et al. 2016; Kashino et al. 2017; Loaiza-Agudelo et al. 2020). However, there are well known differences between the spectral properties of H ii regions and those of high-redshift galaxies (or their local analogs), namely their different location in the [O iii]λ5007/Hβ versus [N ii]λ6584/Hα Baldwin-Phillips-Terlevich (BPT, Baldwin et al. 1981b) diagram (e.g. Steidel et al. 2014; Strom et al. 2017, 2018; Steidel et al. 2016; 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 et al. 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 (<z>=0.08) of their sample.

With respect to integrated spectra, an additional aspect, which may be of great relevance to the abundances of the ionised gas, among others, is the possible inclusion of emission from the diffuse ionised gas (DIG) (e.g. Zurita et al. 2000; Oey et al. 2007) in spectra that include 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...
New calibrations for estimating the N/O ratio

11

Figure 9. The same as Fig.4 but showing the sample of H II regions with T_e-based abundances from Pilyugin et al. (2012) with blue or red dots depending on whether they are located in irregular or spiral galaxies, respectively.

ratios in this low surface brightness component 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 [S ii]/H alpha emission is enhanced in the DIG (more than that of [N ii]/H alpha ratio) with respect to the H II regions (e.g. Galarza et al. 1999; Domgorgen & Mathis 1994). 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 (Zurita et al. 2021a) 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 analogs. Therefore, they have both a higher specific SFR and H alpha surface brightness. The mean DIG emission fraction decreases with increasing 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),6

Figure 10. N2S2 versus N2O2 for the calibration sample from the H II region calibration sample used in this work (Zurita et al. 2021a), 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 Strom et al. (2018) for KBSS galaxies at <z>~2, and for local SDSS galaxies (red solid and dashed lines, respectively); that of Pérez-Montero & Contini (2009) for H II galaxies and H II regions (green line), and the relation derived by Strom et al. (2017) for the H II regions sample of Pilyugin et al. (2012) (blue solid line). The H II regions of the Pilyugin et al. (2012) are also shown with blue or red dots depending on whether they belong to irregular or spirals galaxies, respectively.

Pérez-Montero (2014b), and that from Pilyugin & 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.

6 In fact, the N2O2 is the least sensitive strong-line diagnostic to the DIG and AGN emission (Kewley et al. 2006; Zhang et al. 2017).
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(N/O)-log(O/H) (see e.g. Dopita et al. 2016). 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 ≥ 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 ii] λ6583 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 Zurita et al. (2021a), 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 (p=0.95), with the best fitting function for the log N/O-N2O2 relation being a second-order polynomial:

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

(3)

This relation is valid in the range −1.74 < N2O2 < 0.62, which implies a wide range of ~1.1 dex in log(N/O), with low dispersion in the fitting residuals ($rms \sim 0.09$). These show a positive correlation with the T_e-based oxygen abundance that, if taken into account in the fitting (Eq. 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 ($rms \sim 0.13 - 0.20$ dex) than for N2O2, and their range of validity smaller, especially for N2 that saturates for high values of O2 (≥ ~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, LA20, in the range of validity in common). The N2O2 index is also one of the indices less altered by contamination from the diffuse ionized gas emission (e.g. Zhang et al. 2017) and it is virtually independent on 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 analogs) 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 (https://vizier.u-strasbg.fr/viz-bin/VizieR).

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