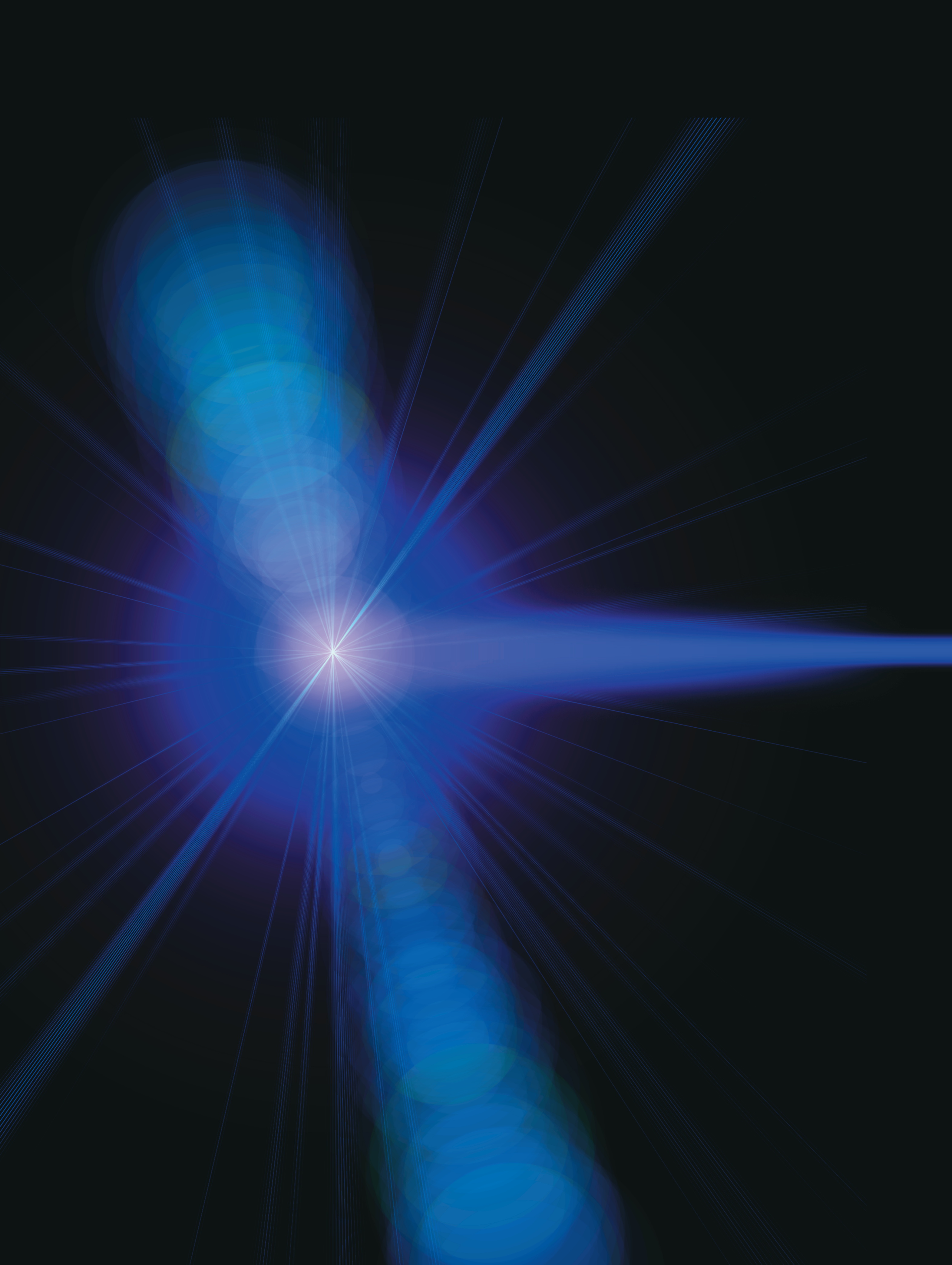

Spectrochemists now have several ways to generate blue light with semiconductor laser diodes, but which one is best for analytical spectroscopy?

Tunable Deep Blue Light for Laser Spectrochemistry

Semiconductor laser diodes have the potential to be used for new applications in analytical instrumentation. The GaN laser diode, which has only been commercially available since 1999, extends the operating wavelengths of laser diodes from the "red" and near-IR to the "deep blue" range. In this article, we describe the properties of GaN laser diodes and compare them with alternative means for generating blue and near-UV radiation.

What's available?

The use of tunable lasers in routine analytical instruments is still very rare. The dye laser was the first type of tunable laser that could cover wide ranges in the optical spectrum. Although it has been extensively and successfully used in research laboratories, its application in routine instruments was fraught with problems, such as lack of robustness and stability, large sizes, high costs, and difficulty in automating procedures.

On the other hand, tunable solid-state lasers are attractive choices for routine analytical spectroscopy. In particular, semiconductor lasers are reliable and relatively inexpensive, and their micrometer dimensions make them interesting light sources for miniaturized analytical instruments and techniques.

Lead-salt laser diodes for the mid-IR spectral range—the fingerprint region of molecular spectroscopy—have been around for more than 30 years. They have been used successfully and are available in commercial instruments. However, lead-salt laser spectrometers must be operated at cryogenic temperatures and often show wavelength drift due to aging ef-

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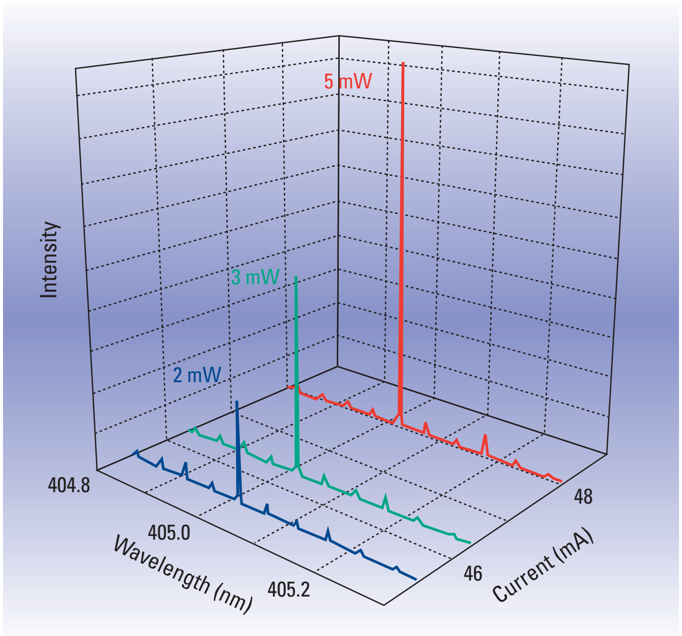

FIGURE 1. The longitudinal mode spectra of a free-running GaN laser diode versus current (power). The spectra were recorded with a high-resolution échelle spectrometer equipped with a charge-coupled device detector.

fects. Although there are several research groups using lead-salt lasers for molecular gas analysis, the drawbacks of these laser diodes have prevented wider application. They will probably be replaced by quantum cascade lasers (QCLs), a new class of semiconductor lasers for the mid-IR range (*1*).

Although QCLs are semiconductor lasers, they operate under a different principle. Whereas laser diodes generate radiation by electron-valence band hole recombinations in bipolar semiconductor devices, quantum jumps among conduction band energy levels in a unipolar multilayer quantum structure produce the stimulated emission of radiation in a QCL. By tailoring the production of the QCL, the wavelength can be set within the range 3.5–17 µm. Significant progress in the development of these novel lasers has made it possible to operate QCLs in a pulsed mode at room temperature and in continuous-wave (cw) mode at liquid nitrogen temperature.

Diode lasers that generate near-IR (AlGaAs/GaAs) and red (InP/InGaAsP) light are very reliable devices. They deliver sufficient cw output power for spectroscopy; have narrow line widths; and can be easily tuned by temperature and current. They are being used for overtone molecular spectroscopy (*2*), atomic spectroscopy (*3*), and especially diode laser atomic absorption spectrometry (DLAAS) (*4*).

In the past, the blue and UV laser radiation necessary for electronic transitions in atoms or molecules has been generated by frequency doubling and sum frequency generation of diode laser light in nonlinear optical media. However, the output powers from these schemes are moderate. Typical powers between tens of nanowatts and several microwatts are generated, depending on the fundamental powers of the laser diodes, which are sufficient for sensitive absorption experiments but not for fluorescence measurements. Moreover, the detection limits for absorption spectroscopy could be improved if higher laser powers were available.

Therefore, when the first GaN laser diodes with a wavelength of ~400 nm were reported, it was an important event for spectroscopists. Unfortunately, at ~$2000 (USD), GaN laser diodes are still expensive because they are produced in small quantities. Therefore, an important question is frequently asked by possible users: Does the GaN laser diode meet my requirements for analytical spectroscopy?

A look at GaN laser diodes

GaN laser diodes (type NLHV500A) are currently available from only one source, Nichia Chemical Industries (Japan). In our studies with these new lasers, we did not open the hermetically sealed housing, nor was an external cavity or optical feedback applied. The diodes were operated with a commercial power supply, which regulates the temperature and the diode current with a precision of ~1 mK and 10 µA, respectively.

Presently, GaN laser diodes can deliver wavelengths from ~390 to ~420 nm at room temperature. The nominal maximum output power is 5 mW, but short operations of up to 10 mW are allowed. Just above the threshold, multilongitudinal mode operation is observed. However, at 2 mW, one particular mode already dominates (Figure 1), although about half of the laser power is still in side modes. In this case, about three-quarters of the power was concentrated in the main mode at 3 mW, while

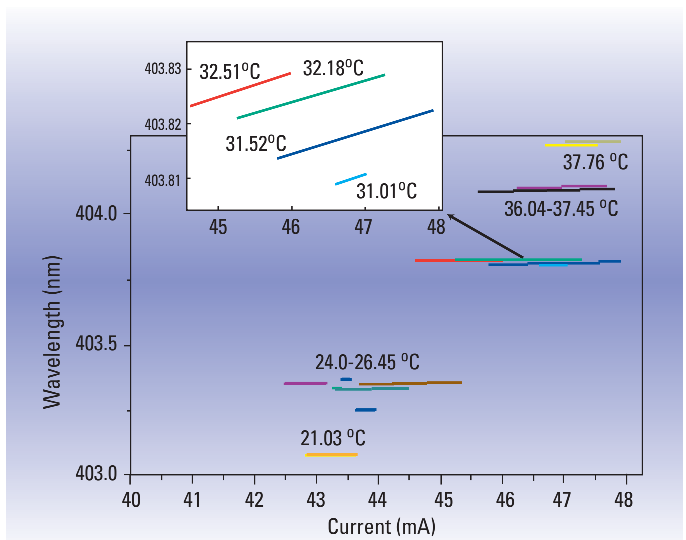

FIGURE 2. The ranges of quasi single-mode operation of the GaN laser diode between 21 °C and 38 °C. Inset shows an enlarged view of the ranges between 31 °C and 32.5 °C.

it was >80% near the maximum nominal power (> 4 mW). At 5 mW, the total power measured was 4.1 mW in the main mode. For comparison, there are near-IR AlGaAs/GaAs laser diodes in which <1% of the total power is in the side modes; commercial InP/InGaAsP laser diodes contribute only a few percent (*5*).

The modes of the GaN laser diode are separated by ~52 pm and distributed over a wavelength range of ~1–1.5 nm, depending on the power. The wavelength of the modes can be tuned continuously over a limited range by changing the diode temperature or the diode current, just as with other semiconductor laser diodes (*5*). The tuning can barely be seen in Figure 1 because the effect was small.

Figure 2 shows all the continuous tuning ranges by current at different but fixed temperatures between 21 °C and 38 °C for one free-running GaN laser diode. There were relatively large wavelength gaps where single-mode operation and tuning of our free-running GaN laser diodes were not possible. Here, a simple reflection from a glass plate or a semi-transparent mirror in front of the laser diode window could force the laser to the desired wavelength (*6*).

Another option is to tune the diode to all wavelengths within its range of operation (gain profile) with a commercial instrument (TuiOptics [Germany]) that applies the feedback from an optical grating. Continuous wavelength tuning at fixed temperatures and current can be obtained by tuning the grating piezoelectrically. However, the mode-hop-free tuning ranges are small (typically, 3.2 pm). They can be increased to ~11 pm by synchronous variation of the diode current and the voltage that is applied to the grating piezoelement (*7*).

As can be seen from the Figure 2 inset, the largest continuous, mode-hop-free wavelength tuning ranges of free-running GaN laser diodes, obtained by current, were ~12 pm. This value is comparable with the ranges obtained with the TuiOptics instrument by synchronous tuning of the diode current and the grating (*7*). However, the tuning ranges of free-running GaN laser diodes are typically much smaller. The dispersion of the continuous tuning is ~4.0 pm/mA. By comparison, the mode-hop-free tuning ranges and the dispersion of AlGaAs laser diodes at 820 nm are typically 250 pm and ~16 pm/mA, respectively.

The overall wavelength tuning range of a single GaN laser diode using the temperature approach is much smaller than that of the well-known AlGaAs or InGaAsP laser diodes. GaN laser diodes can be tuned only a little more than 4 nm by changing the temperature from –35 °C to 45 °C. Red and near-IR laser diodes vary ~13 nm over the same temperature interval. Therefore, careful selection of the GaN laser diodes with respect to the lasing wavelength at room temperature is necessary once the application wavelength is known.

The spectral line width of the free-running GaN laser diode has not yet been measured. However, line width measurements with the TuiOptics spectrometer give a value of ~5 fm. A similar line width can also be expected for free-running GaN laser diodes. In any case, the line width is sufficiently narrow for the analytical spectroscopy of Doppler- or pressure-broadened lines, as well as Doppler-free lines (*7*).

Wavelength modulation is a very important and widely used technique in DLAAS (*3*). Laser wavelength modulation can be easily achieved by adding ac to the diode forward current. It is applied to reduce the $1/f$ flicker noise and suppress nonspecific background in absorption measurements (*3, 8*). To obtain the best signals for wavelength modulation spectroscopy, the amplitude should be between 2.1- and 2.2-times the half-width of the measured line, depending on the shape of the absorption line profile (*8*).

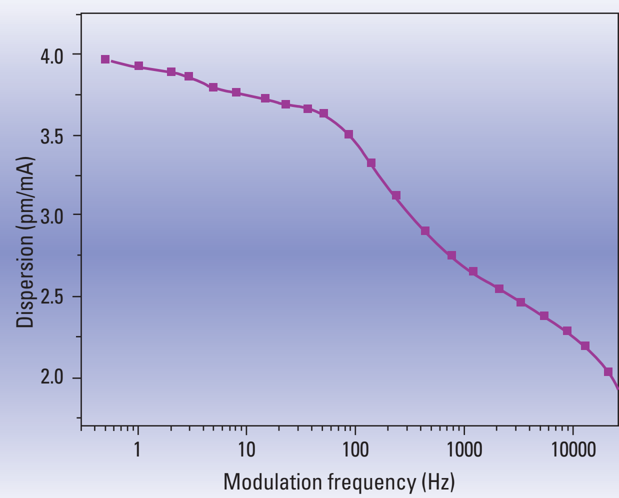

FIGURE 3. Wavelength tuning by the GaN laser diode's current and its dependence on modulation frequency.

Because the mode-hop-free tuning of GaN laser diodes is smaller than with AlGaAs and InGaAsP laser diodes, it is interesting to look at the reduction in wavelength amplitude at constant ac amplitude with a changing modulation frequency. The effect, which is also observed with AlGaAs and InGaAsP laser diodes, is due to reduced heat transfer from the laser chip to the heat sink as the frequency increases. It also affects the wavelength tuning with varying current.

Figure 3 shows the GaN laser diode dispersion and its dependence on modulation frequency. The dispersion, which was ~4 pm/mA at frequencies <1 Hz, was reduced to ~2 pm/mA at 20 kHz. That means that the maximum wavelength amplitude of the GaN laser diodes was only ~6 pm after taking into account the maximum of the mode-hop-free tuning. This could be a problem for analytical spectroscopy.

Figure 4 shows the ^{238}U line at 404.275 nm and the nearby ^{235}U component as measured optogalvanically in a uranium hollow-cathode lamp using a free-running GaN laser diode. Because the $^{238,\,235}$U isotope shift of this line was relatively large (~5 pm), the lines of both isotopes had to be measured in separate scans to have comparable laser intensities at the line centers. The laser was slowly tuned across the line by changing the current, while the intensity of the laser beam was modulated by a mechanical chopper. Lock-in detection was also applied. The signal of the ^{235}U line, shown in the Figure 4 inset, was amplified 100-fold. Note that the spectrum was not normalized to the laser power, which increases toward longer wavelengths. Small asymmetries, particularly in the ^{238}U line, are due to the increase of laser power with current.

It must be stressed that normalization is a problem with free-running GaN laser diodes. Rather, spectral filtering is required using, for example, an interferometer that transmits only the main mode. Another option is using spectral feedback. The feedback from the grating in our TuiOptics instrument reduces the power of all side modes to ~1%, as compared with 15–20% for free-running GaN laser diodes. We expect similar improvements in the spectral purity if optical-feedback from etalons near the laser diode is applied (*6*). It is likely that future GaN laser diodes with higher powers will have better spectral purity. Similar progress occurred after the first InGaAsP laser diodes with wavelengths in the red spectral range were marketed (*3*).

Doppler-free spectroscopy for the $^{115,\,113}In$ 410.176-nm peak using a GaN laser (TuiOptics) has been demonstrated for fluorescence detection in a collimated atomic beam (*7*). No particular problem with limited applicability was reported, because the scan range was small.

Recently, methylcyclopentadienyl manganese tricarbonyl was determined following separation by HPLC and detection by a DLAAS detector looking for manganese in a flame (*8*). About 170 nW of frequency-doubled light from a near-IR laser diode in a 20-mm long $LiIO_3$ crystal was used to measure the 403.076-nm manganese absorption line. The lowest detectable absorption (2×10^{-4}) was given by the shot-noise.

These measurements were repeated using a GaN laser diode with 2 mW of attenuated power. Instead of 1×10^{-5} absorption, which can be expected with sufficient laser power in flames, only 5×10^{-5} absorption was found at the detection limit (*3*). This is a factor of 4 improvement over the near-IR

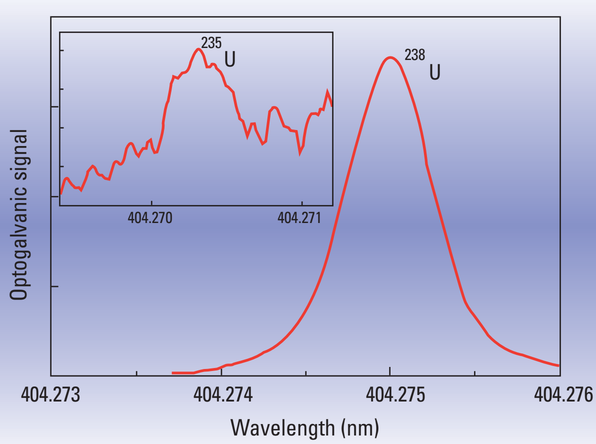

FIGURE 4. Optogalvanic spectrum of the ^{238}U and ^{235}U lines at 404.275 and 404.270 nm, respectively, as measured with a GaN laser diode.

GaN laser diodes can deliver wavelengths from ~390 to ~420 nm at room temperature.

measurement. However, the absorption at the detection limit was still a factor of 5 higher than expected.

The main reason the detection limit is not better is the limited wavelength modulation amplitude. The half-width of the manganese absorption line in the flame was ~6 pm. Therefore, the maximum signal for the manganese line would have required a modulation amplitude >2-fold higher than the maximum amplitudes that can be achieved with GaN laser diodes at modulation frequencies in the kHz range (Figure 3). The relatively small maximum modulation amplitude of the current GaN laser diode is an important restriction for the modulation spectroscopy of atomic and molecular lines.

The laser-induced fluorescence of analytes in liquids will certainly be an important application of GaN laser diodes, because many species absorb in the blue and deep blue spectral range. The spectral purity of the GaN laser diodes is not as important for laser-induced fluorescence in liquids as in atomic and molecular spectroscopy for which narrow lines have to be measured. We believe that the GaN laser diode may be an interesting alternative to gas lasers as detectors for miniaturized separation techniques, such as the CE lab-on-a-chip.

Frequency doubling of near-IR laser radiation

The application of focused near-IR or red light from high-power laser diodes in nonlinear media offers an alternative to the GaN laser diode for generating blue and near-UV radiation. Second harmonic generation (SHG) can occur in crystals in which the critical phases of the fundamental and second harmonic wave are matched, but the process is inefficient. Depending on the crystal, the power of the blue or UV radiation will not be much greater than 100 nW when, for example, 80 mW of fundamental power is applied (*3, 9*). Intracavity SHG can increase the power, but this approach makes the diode laser spectrometer less robust.

An easy and efficient way to produce frequency-doubled light is to use noncritical phase-matching. For example, it is no problem to produce ~4-µW blue light from 80 mW of fundamental power in a $KNbO_3$ crystal (*10*). Unfortunately, the useful wavelength ranges for crystals in noncritical phase-matching are narrow and controlled by temperature tuning. For example, tuning the $KNbO_3$ crystal temperature from –40 °C to 100 °C allows light to be generated only between 419 and 443 nm (*11*).

New optical frequency converters based on periodically inverted microdomain structures in ferroelectric, nonlinear media have been developed (*12*). These systems have a high degree of flexibility and show promise for diode laser spectrometers. Several materials, such as $KTiOPO_4$ (KTP), $LiNbO_3$ or $LiTaO_3$, have been used successfully. These crystals are modified by electrical field poling to obtain periodically inverted domain structures, which are then used to achieve quasi phase-matching (QPM) conditions along the whole crystal (Figure 5a).

In crystals, such as KTP, the largest SHG is achieved if the fundamental and the SHG wave are polarized in the extraordinary direction of the crystal. However, as shown by the red trace in Figure 5b, there is no SHG power at the end of the crystal when there is no inverted structure. The SHG wave generated along the optical paths L_C (also called coherence lengths) also disappears because of destructive interference. However, the power of the SHG wave generated in L_C is conserved if an inverted microdomain follows. The SHG powers accumulate (blue trace in Figure 5b) and almost reach the power level for the theoretical case of perfect phase matching of the fundamental and SHG waves in the crystal (green curve).

The output from a QPM structure is much higher than from crystals with noncritical phase-matching, because the polarization of the fundamental and SHG waves for noncritical phase-matching must be orthogonal. However, the QPM technique enables both waves with the same polarization in the extraordinary direction of the crystal to be used. This direction is known to have the highest nonlinear coefficients of the media. The poling depths on the wafers are up to 3 mm. The length of the domains depend on the extraordinary index of refraction of the crystal and have to be adjusted to the applied wavelength. Heating or cooling the structure slightly changes the lengths of the ferroelectric domains and enables tuning of the QPM structure.

Figure 5c displays the tuning curves of KTP at three different temperatures. Recently, an improved version of a periodically poled KTP for blue light generation was demonstrated (*13*). The period of the domains was 4.2 µm, which was adapted to generate 425-nm light from an 850-nm laser diode. Using optimal optics for laser beam collimation, an SHG conversion of 2–2.5%/(Wcm) was achieved in a single path, and up to 10%/(Wcm) using a double path scheme.

We have used such a periodically poled KTP structure to measure Cr(VI) with a flame DLAAS detector, following separation by HPLC. Without a special lens system to generate a spherical beam and anti-reflection coating on the optical components and the crystal, we obtained 30 µW of blue light at 425 nm with a 9-mm-long KTP structure that received 80 mW of IR laser power. The increased radiation power allowed us to improve the detection limit for Cr(VI) by HPLC/diode laser flame AAS from 30 pg/mL to ~10 pg/mL (*10*).

SHG with QPM structures is an alternative to GaN laser diodes for blue light. The QPM structures are small and robust, and can easily be integrated in diode laser spectrometers. As long as the wavelength range of GaN laser diodes is not extended and their spectroscopic performances are not improved, SHG in QPM structures may be the best choice for powerful laser spectrochemistry in the blue part of the spectrum.

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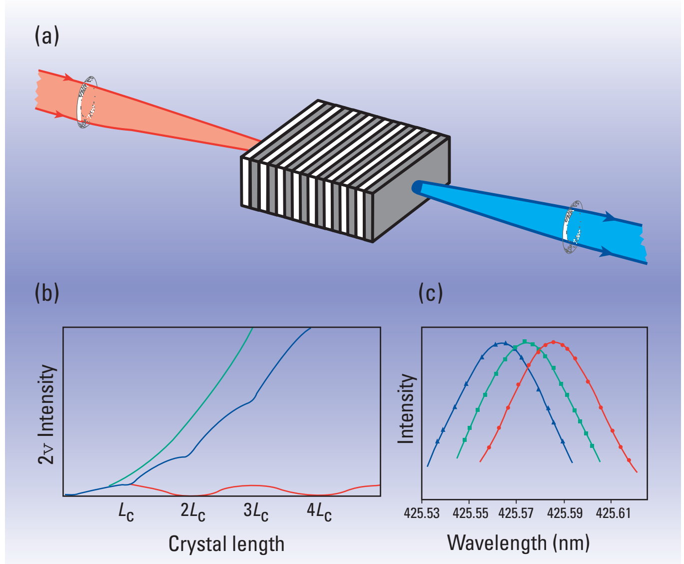

FIGURE 5. Generation of blue laser light in a periodically poled KTP crystal.

(a) Periodically poled optical nonlinear crystal for frequency doubling. (b) The dependence of the second harmonic intensity on crystal length for a structure with periodic poling (blue), without poling (red), and with a perfect phase-match in the whole medium (green). (c) Wavelength dependence of the second harmonic output of a periodically poled KTP crystal at three different temperatures (blue curve is 4.9 °C, green is 5.4 °C, and red is 5.9 °C).

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