

Technical Note

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Single-Shot Biodiesel Analysis: Nearly Instantaneous Typification and Quality Control Solely by Ambient Mass Spectrometry

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Using a simple and easily implemented desorption/ionization mass spectrometry technique, a tiny droplet of biodiesel placed on the surface of a sheet of paper is analyzed directly and nearly instantaneously under ambient conditions. No pre-separation or sample preparation is required, and clean mass spectra are obtained with great simplicity. In the positive ion mode, easy ambient sonic-spray ionization mass spectrometry, EASI(+)-MS, provides typical profiles of the major components of biodiesel samples, that is, either methyl esters (FAME) or ethyl esters (FAEE) of the natural fatty acids and triglycerides (TAG) from residual oil or oil from adulteration. Each FAME (FAEE) or TAG molecule is detected as a single sodiated molecule, $[M + Na]^+$ with relative intensities that correlate well with the known fatty acid profiles of the oil. Using EASI(-)-MS, typical and complementary profiles of free fatty acids (FFA) are obtained, which are detected in their deprotonated forms $[FAA - H]^-$. A general, single-shot approach for biodiesel analysis is therefore described, and samples from different feedstocks, from blends with petrodiesel, or from either methanol or ethanol trans-esterification are readily typified and major parameters of quality accessed.

Biofuels such as ethanol and biodiesel are renewable energy sources of current worldwide interest and one of the most attractive alternatives for replacing rapidly depleting and increasingly expensive petrofuels.¹ Contrary to petrofuels, which display relatively standard compositions, biodiesel composition may vary dramatically as a function of the various feedstocks used worldwide for their production. Biodiesels are made mainly by methanol trans-esterification of the triglycerides (TAG) present in animal fats and vegetable oils, and fatty acid distributions in TAG vary

substantially in terms of carbon length, substitution, and unsaturation level, as a function of the type of animal fat or vegetable oil used for biodiesel production. For instance, TAG from soybean oil is characterized by the predominance of linoleic acid (C18:2) and a substantial amount of linolenic acid (C18:3), TAG from palm oil are characterized by a substantial contribution of palmitic acid (C16:0), and TAG from castor oil contain mainly the distinctive ricinoleic acid (C18:1-OH), which is a 12-hydroxy-9-*cis*-octadecenoic monounsaturated fatty acid bearing a unique hydroxyl substituent on the alkyl chain.

Changes in composition of the resulting mixture of fatty acid methyl esters (FAME) may lead therefore to biodiesels with a broad range of physical chemical properties, which influence their overall efficiency as a fuel (*viz.* cetane number), corrosivity, viscosity, and long-term stability.² For biodiesel standardization and quality control, and to characterize biodiesel blends with petrodiesel (Bn blends), most regulatory agencies require time-demanding measurements via different techniques of several quality parameters, which include FAME or fatty acid ethyl ester (FAEE) and free fatty acid (FAA) contents and the level of residual glycerin and parent animal fat or vegetable oil (measured as tri-, di-, and monoglycerides: TAG, DAG, and MAG). It would be therefore desirable to develop a “as universal as possible” analytical technique able to provide reliable fingerprints of biodiesel for fast typification and quality control.

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We³ and others⁴ have recently shown that direct infusion electrospray ionization mass spectrometry in both the positive and negative ion modes, viz. ESI(±)-MS, allows fast fingerprinting and quality control of biodiesels. In the negative ion mode, ESI(-)-MS provides clear profiles of the FAA, which function as indirect but appropriate natural chemotaxonomic markers for the parent animal fat or vegetable oil. Additionally, ESI(+)-MS fingerprints of biodiesels provide characteristic FAME profiles that also permit typification as well as the detection of major residual contaminants. Accurate quantitation of Bn [*n*% biodiesel and (100 - *n*)% petrodiesel] mixtures by ESI(+)-MS has also been demonstrated.⁴ However, ESI(+)-MS detects FAME or FAEE and residual glycerides via a diverse set of ions that include $[M + H]^+$, $[M + Na]^+$, $[M + K]^+$, $[M - H_2O + H]^+$, and $[M - ROH + H]^+$ as well as dimeric species such as $[M_2 + H]^+$ and $[M_2 + Na]^+$. This “fragmented” and therefore complex information complicates assignment of the ESI(+)-MS fingerprints and makes it less elucidative particularly for biodiesels containing more diverse FAME or FAEE compositions, for biodiesel blends from different feedstocks and for Bn blends.

Recently, a series of new mass spectrometric techniques such as desorption electrospray ionization,⁵ direct analysis in real time,⁶ matrix-assisted laser desorption electrospray ionization,⁷ atmospheric solids analysis probe,⁸ extractive electrospray ionization,⁹ desorption atmospheric pressure photon ionization,¹⁰ and easy ambient sonic spray ionization (EASI)¹¹ have been shown to perform desorption and ionization of analytes directly from natural or auxiliary surfaces at ambient¹² conditions. Among these ambient MS techniques, EASI (originally termed desorption sonic spray ionization¹³) is likely the simplest, gentlest, and most easily implemented. EASI requires no (high) voltage, no UV lights, no laser beams, no corona or glow discharges, and no heating. An EASI source can be constructed and installed in a few minutes from a few simple MS laboratory parts (see Figure 1) and is assisted only by compressed N₂ or air. EASI uses supersonic spray ionization¹⁴ to create very minute droplets, which end up being charged due to the statistical imbalance distribution of cations and anions. The dense stream of the supersonic charged droplets causes analyte pickup from the surface and its prompt ionization.

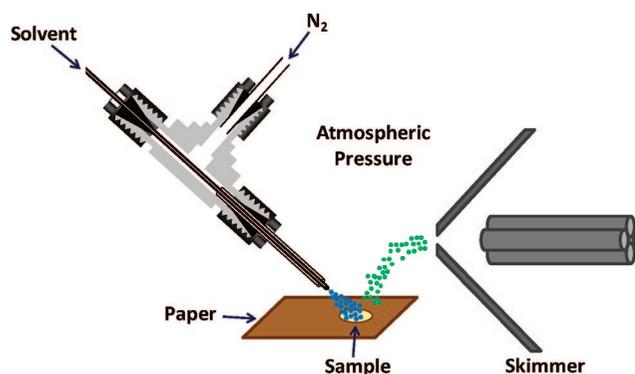


Figure 1. Nearly instantaneous ambient mass spectrometry of pure biodiesel and biodiesel blends. A tiny droplet of the sample (yellow circle) is placed on a paper surface. Major components including FAME or FAEE, and impurities are desorbed and detected by EASI(+)-MS (blue dots) solely as $[M + Na]^+$ ions (green dots) via the supersonic stream of minute charged droplets of methanol. EASI(-)-MS also detects FFA solely as $[M - H]^-$ ions. The sonic spray ionization is assisted only by compressed N₂ (or air), and the EASI source uses a simple Swagelok T-element with appropriate ferrules and tubings for the gas flow and a fused-silica capillary at the supersonic spray exit.

EASI has already been applied with success to different analytes in different matrixes such as drug tablets,¹³ edible oils,¹⁵ perfumes,¹⁶ surfactants,¹⁷ gasoline,¹⁸ and wine,¹⁹ and it has been recently coupled to membrane interface mass spectrometry¹¹ and thin-layer chromatography.²⁰

Here we show that ambient mass spectrometry of a tiny droplet of biodiesel placed on a paper surface via EASI(±)-MS fingerprinting provides nearly instantaneous and clear-cut (“unfragmented”) profiles of both FAME or FAEE and FAA compositions and other major impurities and components. The pre-separation and sample preparation-free EASI-MS data can therefore be used to typify either methanol or ethanol biodiesel samples from different feedstocks and blends to monitor biodiesel production, to provide overall evaluation of quality and to detect adulteration.

EXPERIMENTAL SECTION

Samples. High-purity biodiesel samples from different feedstocks (soybean oil, canola oil, corn oil, castor oil, animal fat, and tallow) were prepared according to an improved trans-esterification procedure described in detail elsewhere.²¹

General Experiment Procedures. EASI-MS fingerprinting was performed in both the positive and negative ion modes using a Q-Trap triple-quadrupole mass spectrometer (Applied Biosystems) equipped with a homemade EASI source, which is described in detail elsewhere.¹³ The main experimental parameters were

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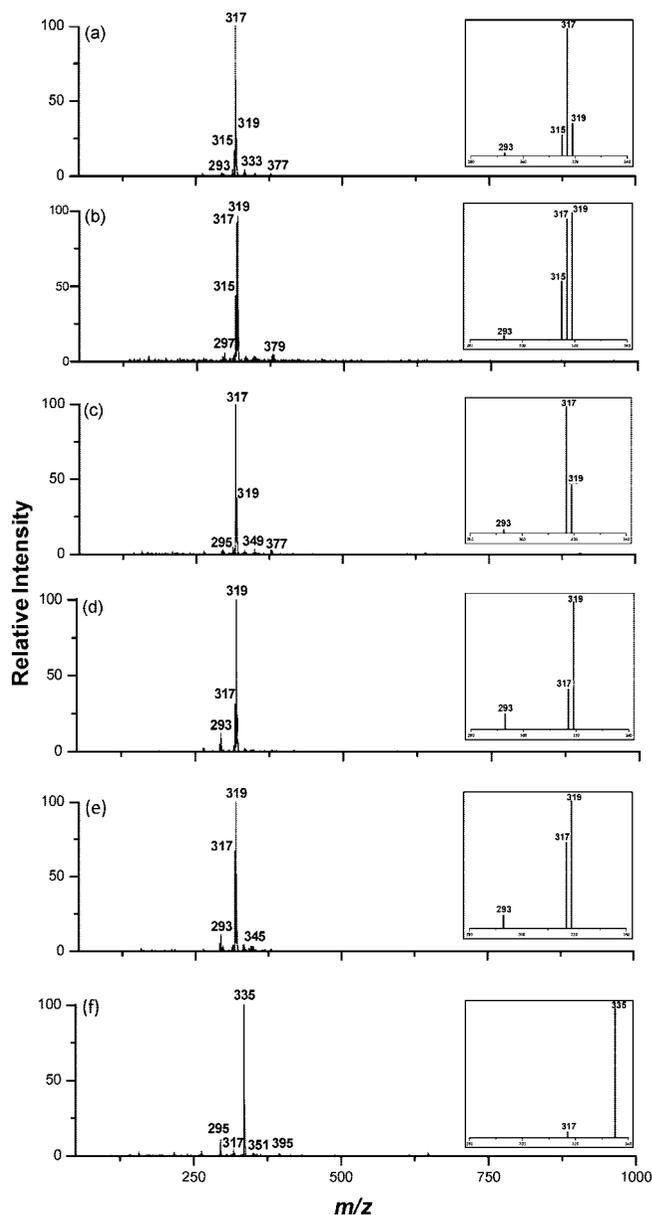


Figure 2. EASI(+)-MS fingerprints of biodiesel samples originating from: (a) soybean; (b) canola; (c) corn; (d) animal; (e) tallow and (f) castor oils and fats. Note the characteristic FAME profiles and the detection of each FAME solely as its sodiated molecule: $[\text{FAME} + \text{Na}]^+$.

as follows: methanol flow rate of $20 \mu\text{L min}^{-1}$, nebulizing gas back pressure of 30 bar, curtain gas pressure of 10 bar, declustering potential of 100 V, tip–paper surface distance of ~ 2 mm, and paper–entrance angle of $\sim 30^\circ$. A tiny droplet of the biodiesel sample ($\sim 5 \mu\text{L}$) was dropped directly onto the paper surface. Mass spectra were accumulated over 1 min and scanned over the 50–1000 m/z range. Spectra were acquired using the enhanced mode of acquisition and by operating Q2 as a linear ion trap.

RESULTS AND DISCUSSION

FAME (or FAEE) Typification. Figure 2 shows typical EASI(+)-MS fingerprints of six representative biodiesel samples prepared via methanol trans-esterification. Note the information-rich and clear-cut (one component = one ion) data obtained as

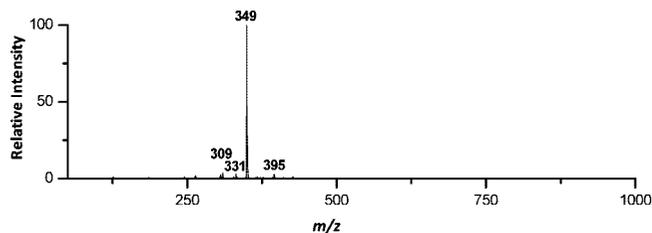


Figure 3. EASI(+)-MS fingerprint of castor biodiesel produced via ethanol trans-esterification. Note the detection of the major $[\text{FAEE} + \text{Na}]^+$ ion of m/z 349 and the 14 m/z shift as compared to the respective $[\text{FAME} + \text{Na}]^+$ ion of m/z 335 from ricinoleic acid (Figure 2f).

each biodiesel sample yields a clean mass spectrum in which each FAME is detected solely as its sodiated molecule $[\text{M} + \text{Na}]^+$. The intensity ratios are also found to reflect the known FA composition of the parent feedstock.²² Note also the great dominance of FAME ions with no detectable ions from impurities, which points to the high purity of the biodiesel samples. To facilitate comparison, the insets in Figure 2 show simplified visualization of the FAME profiles.

The use of a paper surface and the relatively high level of Na^+ in biodiesel promotes ionization of FAME as $[\text{FAME} + \text{Na}]^+$. Sodium adducts are known to form rather stable gaseous species with high resistance to dissociation; hence, no fragment ions are formed and detection operates in a highly desirable “one component to one ion” basis.

The EASI(+)-MS of the soybean biodiesel (a) shows characteristic FAME profile in which the FAME from linoleic acid predominates (m/z 317) with minor $[\text{FAME} + \text{Na}]^+$ ions from esters of oleic (m/z 319), linoleic (m/z 315), and palmitic acid (m/z 293). Corn biodiesel (c) displays a FAME profile similar to that of soybean biodiesel (a), but with a significantly less intense ion of m/z 315. The FAME profiles for animal fat (d) and tallow (e) are also quite similar, but tallow is characterized mainly by a higher m/z 317:319 ratio. The FAME profile for canola biodiesel (b) is characterized by the relatively intense ion of m/z 315. The castor biodiesel (f), as expected, yields a unique profile in which the FAME from ricinoleic acid of m/z 335 greatly dominates.

In Brazil, owing to high availability and relatively low cost, trans-esterification with ethanol may be a viable alternative for biodiesel production.²³ Figure 3 shows, as an illustrative example, the EASI(+)-MS profile of FAEE for a castor biodiesel produced via ethanol trans-esterification. The $[\text{FAEE} + \text{Na}]^+$ ion of m/z 349 (ricinoleic acid) dominates, and the 14 m/z shift as compared to the corresponding $[\text{FAME} + \text{Na}]^+$ ion of m/z 335 (Figure 2f) reveals that ethanol trans-esterification has been used.

Free Fatty Acid Typification. Figure 4 illustrates a typical EASI(-)-MS fingerprint for a sample of animal fat biodiesel. When operating in the negative ion mode, the major species detected are the FFA, which are transferred to the gas phase solely in their

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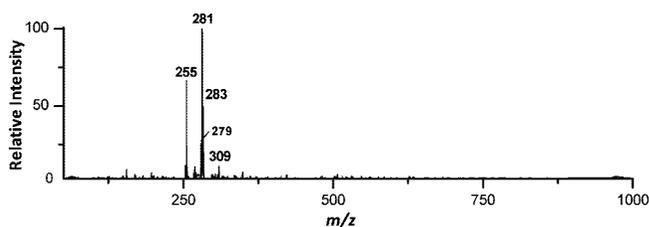


Figure 4. EASI(-)-MS fingerprinting of animal fat biodiesel. Note the typical profile of FFA detected as their deprotonated molecules $[M - H]^-$. The main four anions correspond to palmitic acid (m/z 255), linoleic acid (m/z 279), oleic acid (m/z 281), and stearic acid (m/z 283).

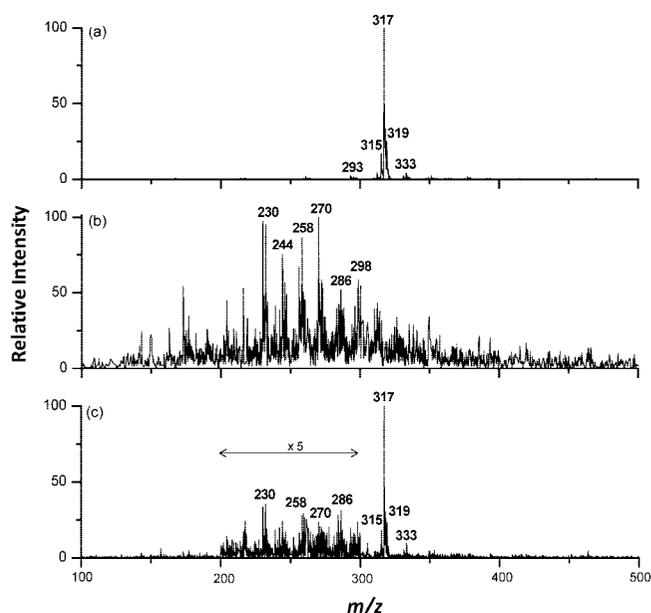


Figure 5. EASI(+)-MS fingerprints of (a) soybean biodiesel, (b) petrodiesel, and (c) a B2 biodiesel/petrodiesel blend.

intact deprotonated forms $[FFA - H]^-$. Characteristic and complementary EASI(-)-MS fingerprints also with “unfragmented” profiles of FAA are therefore obtained. Reasonably accurate FAA quantitation (not shown) is also possible particularly via the use of internal standards such as, for instance, an unnatural C17 fatty acid.

EASI needs no polarity switching since it employs no voltage to create both negative and positive ions and modern mass spectrometers can be instantaneously and automatically switched from the positive to the negative ion mode. Both EASI(\pm)-MS fingerprints can therefore be rapidly obtained for more secure, cross-checked typification and quality control (impurities other than FAA should also be detected) of biodiesels.

Bn Mixtures. Biodiesel is being commercialized worldwide in blends with petrodiesel. In Brazil, the B2 blend (2% biodiesel and 98% petrodiesel) is currently being employed, and different techniques are being evaluated to perform fast and reliable quantitation of Bn blends.²⁴ To evaluate the ability of EASI-MS fingerprinting to characterize Bn blends, the data of Figure 5 were collected. Figure 5a shows the EASI(+)-MS of a pure soybean biodiesel sample (B100) with its characteristic FAME profile.

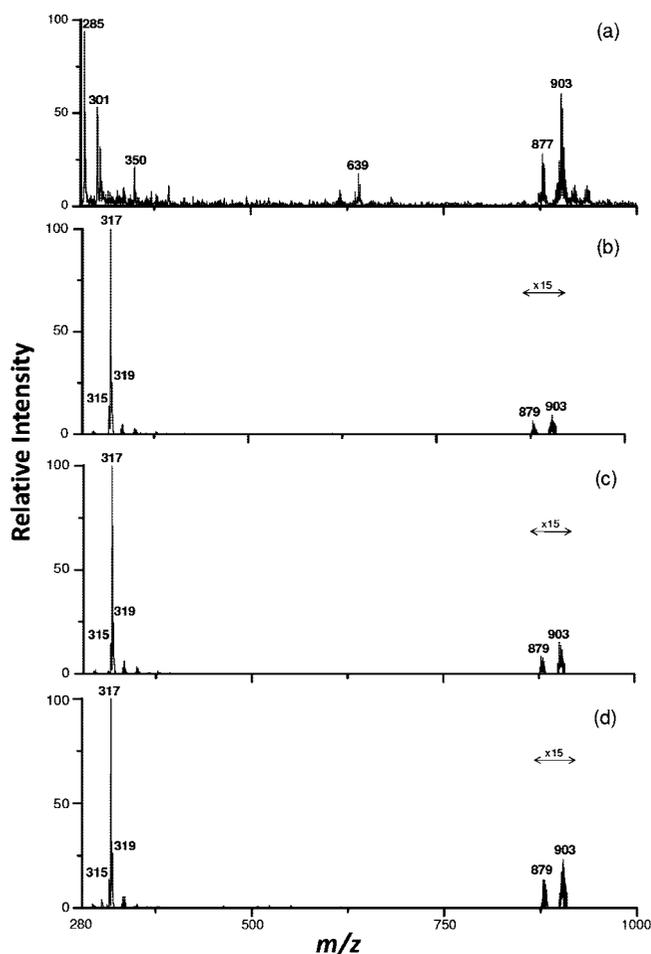


Figure 6. EASI(+)-MS fingerprints of soybean oil (a) and of high-purity soybean biodiesel doped with (b) 2, (c) 5, and (d) 10% of the parent soybean oil.

Figure 5b shows the fingerprint of pure petrodiesel (B0), which displays a set of ions corresponding to the ionization of characteristic markers of petrofuels,¹⁸ that is, a homologous series of alkyipyridines.²⁵ Figure 5c shows the ESI(+)-MS fingerprint of the respective B2 blend. Note that the spectrum not only clearly characterizes the sample as a Bn blend but also reveals the type of biodiesel used (soybean) via the characteristic profile of FAME ions of m/z 315, 317 (main), and 319.

Quality Control. Figure 6 shows the typical EASI(+)-MS fingerprints of pure soybean oil (a) and soybean biodiesel doped with the parent soybean oil in increasing amounts. Here we simulated a low-quality biodiesel (incomplete trans-esterification) or a possible practice of biodiesel adulteration via mixing of the parent feedstock.²⁶ The EASI(+)-MS fingerprint of pure soybean oil (a) is also clear and elucidative since it detects the TAG exclusively in their $[TAG + Na]^+$ forms and with a TAG profile that is characteristic of soybean oil: PLL (m/z 877.8), PLO (m/z 879.9), POO (m/z 881.9), LLLn (m/z 899.8), LLL (m/z 901.7), LLO

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(m/z 903.9), OOL (m/z 905.9), and OOO (m/z 907.9).²⁷ Note also the cluster of less intense ions of sodiated DAG centered at m/z 639. When soybean oil is added to soybean biodiesel (Figure 6b–d), the EASI(+)-MS fingerprints readily identifies and estimates the oil content since both the characteristic set of FAME ions from soybean biodiesel and TAG ions from soybean oil are clearly detected at nearly quantitative ratios.

CONCLUSION

Nearly instantaneous ambient mass spectrometry via EASI(\pm)-MS fingerprinting of a tiny droplet of biodiesel placed on a paper surface provides clean matching, “unfragmented” profiles of both the FAME (or FAEE) and FAA compositions of the sample. With no pre-separation and no sample preparation, these fingerprints can be used with confidence to perform laboratory or on-site typification of biodiesel samples from many different feedstocks, to monitor biodiesel production, to evaluate quality and detect adulteration, and to characterize Bn blends. Reasonably accurate quantitation of FFA and Bn blends²⁸ is also possible. Long-term ongoing studies in our laboratory including seasonal effects, with the goal to analyze a larger set of “real-world” samples from different production sites, geographical origins, and methods of production (including used frying oil) and for different biodiesel blends from various feedstocks indicate the robustness of the EASI(\pm)-MS fingerprinting method to typify biodiesel and to access major parameters of quality control. The initial results also indicate its ability, after chemometric processing, to discriminate

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multicomponent biodiesel blends. The MS detection of each FAME or FAEE and TAG as single $[M + Na]^+$ ions greatly facilitates oil and biodiesel typification and permits therefore not only the quantitation of Bn and biodiesel/oil mixtures but also the identification of the type of biodiesel and oil present in such mixtures. EASI(\pm)-MS fingerprinting seems to provide therefore a general and rapid single-shot technique for biodiesel typification, process monitoring, and quality control, being able to evaluate major parameters required for biodiesel specification.

Although mass spectrometers of considerably reduced sizes and costs (as low as average GC or LC instruments, for instance) are already commercially available, miniature mass spectrometers able to operate with ambient ionization techniques and of very reduced sizes and weights (less than 10 kg) are being developed, and are being made continuously more compact, versatile,²⁹ and hopefully, less expensive. For such miniature mass spectrometers, EASI (owing to its simplicity and no power requirement) seems to be the most suitable and easily implemented ionization technique. Lighter and more affordable hand-portable EASI mass spectrometers may soon be available for on-site, nearly instantaneous, single-shot fingerprinting of biodiesel and Bn blends.

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