DIPLOMARBEIT / DIPLOMA THESIS

Titel der Diplomarbeit / Title of the Diploma Thesis

Use of drift-tube ion mobility spectrometry to enhance HPLC-TOFMS analysis of phenolic extracts

verfasst von / submitted by

Marian Došen

angestrebter akademischer Grad / in partial fulfilment of the requirements for the degree of

Magister der Pharmazie (Mag.pharm.)

Wien, 2016 / Vienna, 2016

Studienkennzahl lt. Studienblatt / degree programme code as it appears on the student record sheet:	A 449
Studienrichtung lt. Studienblatt / degree programme as it appears on the student record sheet:	Diplomstudium Pharmazie UniStG
Betreut von / Supervisor:	ao. Univ.-Prof. Mag. Dr. Gottfried Reznicek

Statutory Declaration

I declare that I have authored this thesis independently, that I have not used other than the declared sources/resources, and that I have explicitly marked all material which has been quoted either literally or by content from the used sources.

Vienna, ______________________ ______________________________

Date Signature

Eidesstattliche Erklärung

Ich erkläre an Eides statt, dass ich die vorliegende Arbeit selbstständig verfasst, andere als die angegebenen Quellen/Hilfsmittel nicht benutzt, und die den benutzten Quellen wörtlich und inhaltlich entnommenen Stellen als solche kenntlich gemacht habe.

Wien, am ______________________ ______________________________

Datum Unterschrift

未練なく散も桜はさくら哉
without regret
they fall and scatter…
cherry blossoms

for 無禅

Acknowledgment

The continuous support of the whole working group of Assoc. Prof. Dr. Stephan Hann at the Division of Analytical Chemistry at University of Natural Resources and Life Sciences, Vienna was much appreciated. Special thanks to Dr. Tim Causon and Assoc. Prof. Dr. Stephan Hann for their guidance, patients and the provided possibility to work with them.

I would like to thank ao. Univ. Prof. Dr. Gottfried Reznicek from the Department of Pharmacognosy, University of Vienna for his support of this work in the first place.

Furthermore I would like to express my gratitude to my father, who if he would be still with us, would have liked my effort to process the topic at hand, after all he was the one who told me how to use my brain.

Zusammenfassung

Die vorliegende Arbeit beschäftigt sich mit der Evaluierung eines, zwar nicht ganz neuen, aber erst vor einiger Zeit kommerziell zugänglichen Versuchsaufbaus. Es handelt sich dabei um Ionen mobilitäts Spektrometrie (IMS), die als Zusatzelement in einem gängigen quadrupol-Flugzeit-Massenspektrometer (QTOF) verbaut ist und jeweils mit Flüssigchromatographie (LC) gekoppelt wird. Die IMS-Einheit basiert dabei auf dem Prinzip der Drift-Zeit Auswertung und soll die Ionen nicht nur nach ihrem Masse zu Ladungsverhältnis sondern auch nach ihrem Form zu Ladungsverhältnis trennen. Driftzeit ist jene Zeit die ein Ion braucht um eine gewisse Strecke innerhalb der IMS-Einheit zu passieren und hängt von verschiedenen Parametern ab die innerhalb der Arbeit erklärt werden. Durch die Arbeit soll versucht werden den Nutzen dieser Methode für die Analyse von Pflanzenextrakten mit einem hohem Gehalt an phenolischen Sekundärstoffen, wie zum Beispiel Flavonoiden abzuschätzen. Um über geeignete Proben zu verfügen, die in gleichbleibender Qualität vorhanden sind und ohne großen Aufwand vorzubereiten waren, wurde Wein als Prototyp eines phenolischen Pflanzenextrakts gewählt.

Durch wiederholte Messungen gleicher Weinproben wurde die Wiederholgenauigkeit und die Zuverlässigkeit der Ergebnisse überprüft. Vor allem in Hinblick auf die Datenverarbeitung wurde versucht LC-IM-QTOF und LC-QTOF allein zu Vergleichen. Um dies zu ermöglichen wurden drei verschieden Weine durch Gruppierung der extrahierten Daten auf ihr Unterschiede geprüft. Im weiteren Verlauf der Arbeit wurde hoher Wert auf die Kalibrierung des Gerätes hinsichtlich der Drift-Zeit gelegt und der Stoßquerschnitt (CCS) für einige der Ionen ermittelt. Im letzten Teil der Arbeit wurde versucht die zusätzlichen Daten die durch die IMS zu Verfügung stehen zu nutzen um Probleme bei der Ermittlung von qualitativen Aussagen zu einzelnen Ionen aufzuzeigen.

Letztendlich kommt die Arbeit zu dem Schluss, dass die zusätzlichen Daten die durch die Driftzeit Messung zu Verfügung stehen durchaus sinnvoll für eine weiter in die Tiefe gehende Analytik sind. Es bedarf jedoch noch einiger Optimierung der vorhandenen Methode um den vollen Nutzen aus dem Experiment zu erhalten.

Abstract

The present work deals with the evaluation of a relatively new commercially available instrument. The instrument concerned is a drift-tube ion mobility (IMS) combined with a quadrupole time-of-flight mass spectrometer (QTOF). The IMS is based on the principle of drift time ion mobility separation of ions relating to their shape-to-charge of ions. Drift time is the time an ion needs to pass through the IMS drift tube and is determined by different parameters, that are explained within the work. Throughout the work, it is a primary goal to estimate the value of this approach for the analysis of plant extracts containing a high concentration of phenolic secondary metabolites (e.g. flavanoids). To have suitable tests samples, which were easy to obtain and required low cost preparation, wine was chosen as a prototype of phenolic plant extracts.

The repeatability and the reliability of the results were checked by repeated measurements of the same wine samples. Above all comparison of the data processing of liquid chromatography in combination with ion mobility-time-of-flight-mass spectrometry (LC-IM-QTOF) and LC-QTOF alone, was aimed at. To allow this, three wines were checked by alignment of the extracted data for differences. High value was placed into the other part of the work; the calibration of the device concerning the drift time and the collisional cross section (CCS) determination for some of the ions. In the last part of the work, the additional data acquired by the IMS is used with some qualitative examples from targeted compounds to demonstrate the type of information that can be included in a full-scale LC-IM-(Q)TOF workflow.

A major conclusion of this work is that the additional separation and feature alignment utility of IMS will be valuable for both targeted and (possibly) non-targeted analytical workflows for phenolic extracts. Nevertheless, some optimization and investigation into further elements are still required. Some suggested further work to address these issues is suggested at the end of this thesis.

Contents

List of Figures

List of Tables

1. Introduction

Ion mobility spectrometry in combination with mass spectrometry (IMS-MS) as a tool for solving analytical problems is becoming more common recently due to the fact, that new instruments aiming to offer increased measurement selectivity are emerging on the market which are ready for routine usage [1].

This thesis will deal with the development of analytical work flows to separate and characterize small molecules, using this approach on a newly available commercial instrument with a focus on polyphenolic compounds from plants. In order to broadly assess the potential of this technique for this application, reproducible samples (red wine) containing a wide variety of phenolic substances will be used as a test subject. The benefit of some red wine compounds for human health have been intensively studied and described in numerous publications and books and there is a still ongoing discussion about it throughout the scientific community [2, 3]. This discussion is not only present for wine, it is present for many plant compoundings and the healing or harming principles often are not fully understood, although some of them are used for centuries by humankind.

Plant extracts and fermentations are complex mixtures of chemical compounds and resolving their structures and determination of phenolic profiles requires much effort as knowledge continues to grow in this area. The last decades of analytical chemistry introduced mass spectrometry (MS) and in addition, high resolution mass spectrometry on a routine basis, which made it possible after chromatographic separation, to screen through a high number of samples. Such screenings brought an astonishing flow of detailed information for substances present in biological systems in general. To develop a general analytical workflow for this purpose, high-quality annotation and alignment of features across samples are essential requirements.

1.1. Polyphenols

Exact definitions for secondary plant metabolites are not always easy to provide due to the fact, that plant-derived substances encompass such a wide and structure rich environment. Major groups of compounds are defined by their functional groups or backbone structures from which they are built, for example as is the case for terpenoids. When it comes to polyphenols, however, there are also some main structures grouped together according to chemical properties and polymerization grade. The review of [4] presents a good overview of which kind of polyphenolic structures one could be confronted with, when trying to resolve a sample of plant extracts such as wine. Some of these substances classes are shown in **Figure 1.1**.

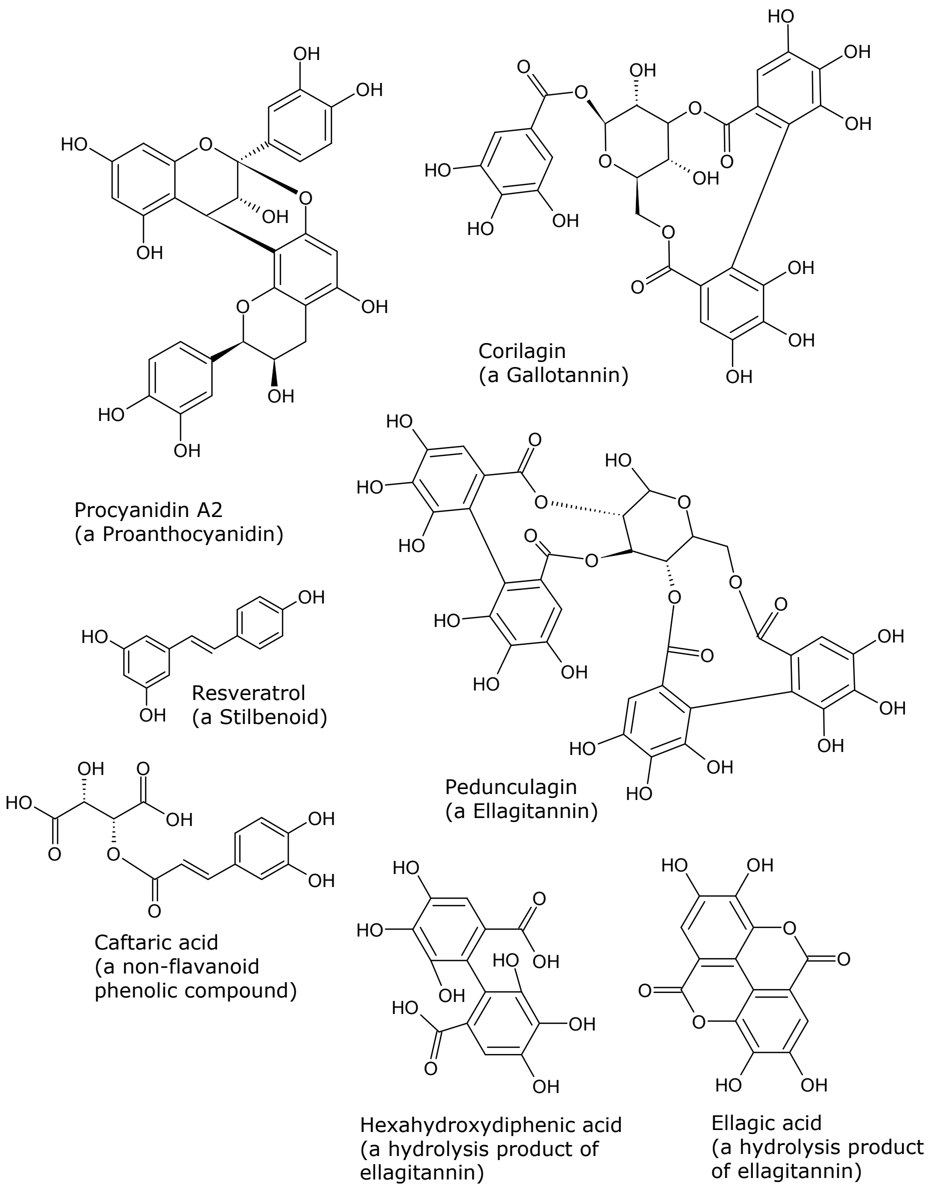


Figure 1.1.: Examples of compounds found in wine representing various classes of polyphenols.

1.1.1. Flavonoids

Flavonoids are polyphenolic secondary plant metabolites, which are ubiquitous for all higher plants. Their purpose in nature seems to be for coloring flowers and fruit to attract or repel insects, as well as protecting plants from the adverse effects of UV-light and from herbivores or insects [5]. From the viewpoint of organic chemistry

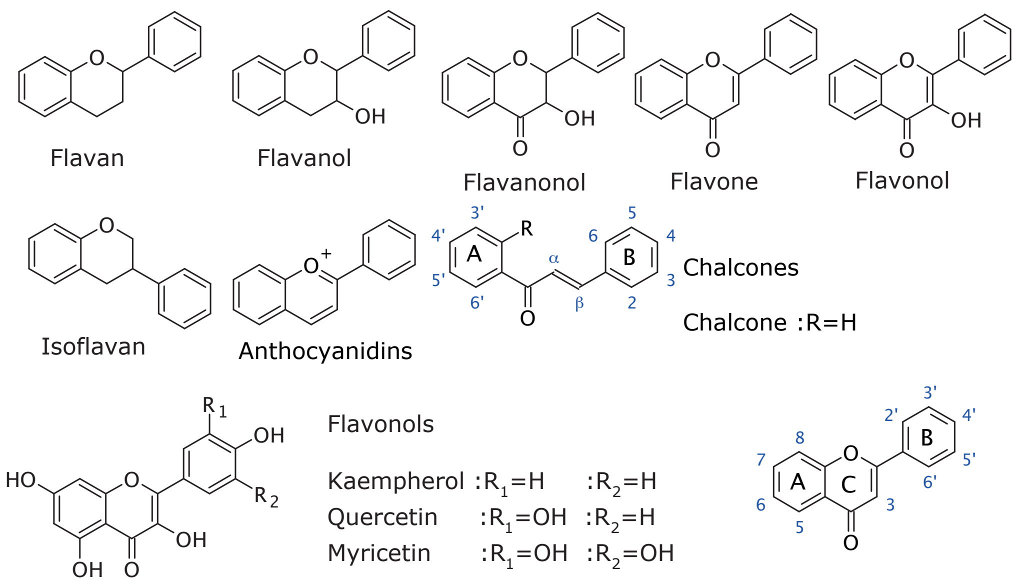


Figure 1.2.: Common flavonoids and used nomenclature numbering pattern.

and nomenclature, the flavonoids are separated in different groups, based on their grade of oxidation and type of bonding. All groups resemble the same basic pattern of the flavan, a 3,4-dihydro-2-phenyl-2H-1-benzopyran, according to International Union of Pure and Applied Chemistry (IUPAC) nomenclature. The antioxidant properties of flavonoids correlate with their ability to scavenge radicals, which corresponds mostly to the position and the number of hydroxyl groups bound to the rings [6]. In **Fig. 1.2** the basic classification of flavonoids are shown, but considering that over 8000 different flavonoids up until 2006 have been characterized, it is merely an overview.

Many flavonoid drugs are used in herbal medicine with a long and successful tradition. However, not always the exact substance or the combination of substances that form the healing principle is known or comprehensively confirmed. Polyphenols such as anthocyanidins, as well as flavonoids, have been proposed as being responsible for these effects primarily due to their antioxidant properties [7]. Newer investigations on anti-inflammatory properties of different flavonoids, such as quercetin show, that they interact with arachidonic acid pathway enzymes and tumor necrosis factor kappa b pathway enzymes, which are important targets in drug development [8] and lead to ongoing research and testing of their activities, using different assay methods [9–11].

Keeping in mind, that flavonoid compounds could lead to new pharmaceutical drugs in fighting disease connected to inflammation processes, such as cancer or arteriosclerosis [12–14], the development of new powerful analytical methods in separation and identification is a crucial step in the discovery process. This is not only true for extensive qualitative analysis, with the aim to find new structures or confirm the structures of the huge amount of features, that can be extracted from mass spectrometry data, but also for reasons of quality control and quantification of target compounds.

Emphasizing on the development of a method for liquid chromatography (LC) hyphenated with ion mobility spectrometry (IMS) and high resolution time of flight mass spectrometry (TOF), using an additional quadrupole for fragmentation (LC-IMS-QTOF) for the analysis of wine samples, in addition to methods for origin determination and quantification, (carried out at University of Natural Resources and Life Sciences, BOKU-Vienna, Department of Chemistry, Division of Analytical Chemistry), different aspects of method development and feature annotation will be considered to enrich existing work flows [15].

1.1.2. Polyphenolic and flavonoid content in Wine

Concerning the polyphenolic and flavonoid content in wine, there are many publications dealing with how these compounds influence the taste or health impact of wine [16–18]. For this thesis, a brief overview of substances known to be found in common red wine, will be given, later in the results section some of these compounds will be targeted in detailed qualitative examples.. These substances have been chosen to show the possibilities of identification and annotation that the proposed analytical workflow presented in this work, provides **Table 1.1**.

Table 1.1.: Compounds present in wine, chosen for closer investigation.

Compound	Sum formula	Molecular Mass [$g\,mol^{-1}$]	Exact Mass
Kaempherol	$C_{15}H_{10}O_6$	286.24	286.0477
Catechin	$C_{15}H_{14}O_6$	290.27	290.0790
Epicatechin	$C_{15}H_{14}O_6$	290.27	290.0790
Caftaric acid	$C_{13}H_{12}O_9$	312.23	312.0481
Miquelianin	$C_{21}H_{18}O_{13}$	478.36	478.0747
Castavinol	$C_{26}H_{30}O_{14}$	566.50	566.1636

1.2. Analytical methods for wine analysis

For the separation and detection of polyphenolic compounds from plants, high performance liquid chromatography (HPLC) separations, with their different detection methods, are the state of the art technology. HPLC combined with mass spectrometry is already considered the benchmark tool for characterization and separation of plant extracts [19]. However, there is still room for improvement for a number of issues, such as the separation and identification of isobaric or stereo-isomeric compounds, especially within the group of flavonoids, as they are compounds with only slight variations in structure, which could nevertheless exhibit different biological activity.

Therefore, development of techniques that are able to resolve the complexity of samples with a large number of different, but structurally similar components, is important both in the search for new bioactive compounds and for broad scale comparisons of different extracts (e.g. authenticity determination).

1.2.1. High performance liquid chromatography (HPLC)

When it comes to identification, molecules must be chromatographically separated in order to yield a robust identification parameter and allow detection of constituent components with a detector. HPLC has been a mainstay for some time now and, together with gas chromatography, remains a primary method of choice for the separation of complex samples. The wine samples at hand in this study can be formally seen as a liquid alcoholic plant extract, where the substances of interest are moderately polar organic molecules, that show good separation on reversed-phase HPLC columns. Reversed-phase HPLC separation is very suitable for such applications due to the fact, that a wide polar and apolar range of molecules, is present in such samples and is now the most commonly used method for phenol analysis [20].

HPLC itself is a very effective separation technique, using numerous chemical and physical principles for separation, depending on the column and mobile phase employed. The separation principle of reversed-phase HPLC is the interaction of apolar molecules with the apolar stationary phase material (typically silica derivatized with hydrophobic groups) and an organic-aqueous mobile phase, such as acetonitrile/water. HPLC has a wide variety of applications and a vast amount of different setups, the exact setup used for the analysis executed in this thesis, will be explained in the experimental section in detail, however, it is important to note, that the coverage of the polarity range in case of plant extracts is always a problem.

With the setup at hand, the retention of the heavier phenolic compounds with multiple hydroxy groups and the antocyanidins (because of their positive charge), will be very weak, so that they all appear badly separated before the first two minutes of the chromatography, which are not reliably usable for further annotation. Chromatography is always a compromise between time, separation quality and the amount of different substance groups covered. The approach used for the wine analysis in this case, was focused on good separation of a mix of standards, in the mass range of 160-320 $g\,mol^{-1}$, that are flavonoids or phenolic compounds with a not too large polarity range covered.

This lead to the expectation, that similar compounds would be found in the retention time range of the standards.

1.2.2. HPLC-MS

Coupling of HPLC with MS enables the possibility to measure mass information of separated compounds in an on-line-fashion. A wide variety of mass spectrometry principles can be used including ion trapping, quadrupole filtering, time-of-flight and Orbitrap mass analyzers. In this thesis, a time-of-flight (TOF) mass analyzer was employed. In this type of mass analyzer, ions are accelerated in a flight tube and the time required to reach the detector is used to calculate the mass-to-charge-ratio.

1.2.3. Ion mobility spectrometry mass spectrometry (IMS-MS)

Together with drift time IMS, which will be discussed in detail as it is the instrument used in this thesis, differential-mobility spectrometry and traveling wave IMS with a lot of different setups, are used to try to solve analytical problems. The review of [1] provides an excellent overview of IMS-MS principles. HPLC coupled to ion mobility spectrometry-mass spectrometry (IMS-MS) is suggested in this work, to be a potentially suitable technique for the analysis of phenolic extracts [21], as it offers the possibility to bring a new dimension, the drift time (related to the shape-to-charge-ratio of an ion) into account for compound separation and identification.

1.2.4. Drift tube IMS theoretical background

The theory of gaseous ion mobility, is part of the kinetic theory of gases and its application for IMS-MS was developed in the 1950s-1970s and further extended into research instruments in subsequent years [22–25].

In the case of ion transport in a drift-tube environment, the gas phase mobility of an ion, therefore is proportional to the electrical field strength E and inversely proportional to the pressure of the drift gas p and the drift time velocity v_d. Where the drift time t_d, then is directly proportional to the ratio of field strength divided by the pressure E/p [22, 25]. Measuring the drift time as an analytical parameter is thereby used, to characterize ions and calculate collisional cross sections for comparability and is the primary aim of this analytical approach. In the case of IMS-TOF, the additional measuring of masses by high resolution mass spectrometry, enables detection and further information to be derived. Equation (1.1) represents the fundamental idea behind it, in a mathematical way.

$$v_d = KE \tag{1.1}$$

The additional possibility of adding collision energy for fragmentation, which is done in an alternating frame manner, provides even more flexibility for the analytical workflow. Alternating frames in this case means, due to the fact that ions pass the drift tube as packages similar to the way they are introduced into the flight tube, collision energy is switched on and then off again, for a certain amount of transient. This brings in the possibility to product lock ions to certain drift times and be able to tell exactly which ion produces which fragments, without being forced to lock the quadrupole to a certain mass range. To make the concept clearer, it will be discussed in detail in **Section** 3.6.

1.2.5. Concept of the collisional cross section

As mentioned above the drift time t_d is a function of ion mobility, pressure and field strength and therefore correlates to the parameters of our method and device only. Using the drift time and mass to charge information derived from drift-tube IM-MS measurements, calculation of the momentum transfer integral, according the fundamental zero-field equation, allows a so-called collisional cross sections (CCS) for a given ion to be calculated.

CCS itself can be seen as a representation of an ion-neutral complex derived from a simple model of hard spheres colliding. The CCS value of an ion in a given collision gas for the most part, depends on the radius (the ion is seen as a sphere) and reduced mass of the ion. The theory of gaseous ion mobility ultimately brought forth an equation by Mason and Schamp [22], relating the ion mobility to a CCS value (or momentum transfer integral, Ω), charge state Q, temperature T, drift gas density N and reduced mass μ of the ion colliding with the drift gas molecules (1.2).

$$K = \frac{3}{16}\sqrt{\frac{2\pi}{\mu kT}}\frac{Q}{n\Omega_D} \tag{1.2}$$

For the determination of CCS values a simple approach called stepped-field method, can be used. The drift tube voltage difference is changed in a number of short time steps differing by a known voltage "'step"' (for example from 1700 V to 1100 V in 6 steps differing by 100 V each), while a substance of interest is directly infused into the system. Longer run-times make the measurements more precise, but 2.5 minutes where used in the methods in this thesis and the precision was kept inside 1 %. To then calculate the CCS value, the temperature and pressure of the used drift gas as well as the length of the drift tube, must be known. Then the CCS value can be acquired from a drift time t_d against reciprocal field strength difference $1/\Delta V$ plot, which turns out to be linear in a certain field strength range, because t_d is directly proportional to the E/p ratio. The intercept of the linear function is used, to determine the minimal time t_0 an ion needs to pass the drift region, hence its a correction of the actual t_d, according to the ion optics, much like the concept of dead volume in chromatography.

Using the corrected t_d and the known parameters of the instrument, CCS values can then be calculated simply by rearranging **Equation** 1.2 into **Equation** 1.4. To be able to compare different measurements on different instruments, additionally the reduced mobility K_0, is commonly calculated by **Equation** 1.3 and can be seen as the ion mobility at standard gas density n_0, temperature and pressure ($T_0 = 273$ K and $p_0 = 1013$ mbar).

$$K_0 = K\frac{n}{n_0} = K\frac{T_0}{T}\frac{p}{p_0} \tag{1.3}$$

$$\Omega_D = \frac{3}{16}\sqrt{\frac{2\pi}{\mu kT}}\frac{Q}{nK_0} \tag{1.4}$$

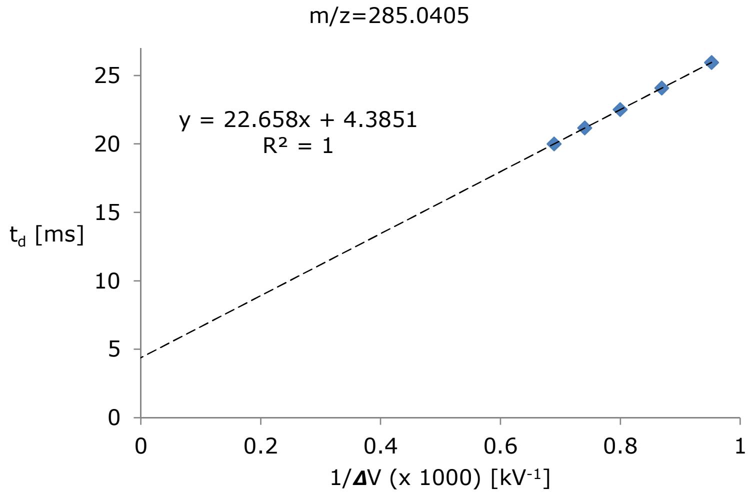


Figure 1.3.: Stepped-field method plot for the $[M-H]^-$-Ion of kaempherol, with a CCS value of 166.9 $\AA^2$ and the t_d [ms] at different field strength.

As mentioned before, the stepped-field approach needs the drift-tube voltage to be changed while the system is running, this makes it impossible to use the approach for calculating CCS values, when the sample is introduced as a chromatographic peak of narrow width. The field strength could not be stepped, according to every substance eluting from the chromatography, it is self-evident, that there would not be enough time to accomplish this.

To still be able to calculate the values for all features from a sample-run in HPLC-IMS-MS mode, a single-field approach is used, that is basically a calibration-function of CCS values, determined from the same calibrant mixture, used for the mass calibration of the system. The CCS values of the ions in the calibrant solution are measured with a stepped-field method before the actual sample run and the calculated results are entered into a calibration table, that subsequently allows assignment of CCS values for all found features according to a linear calibration function. This approach was developed by the instrument manufacturer Agilent Technologies, and the calibration table used for the actual measurements can be reviewed in the Appendix.

The fact that t_d and the CCS value is directly related to the mass of an ion makes the ordering in **Fig. 1.4** obvious, however, the shape of an ion makes the small, but measurable difference.

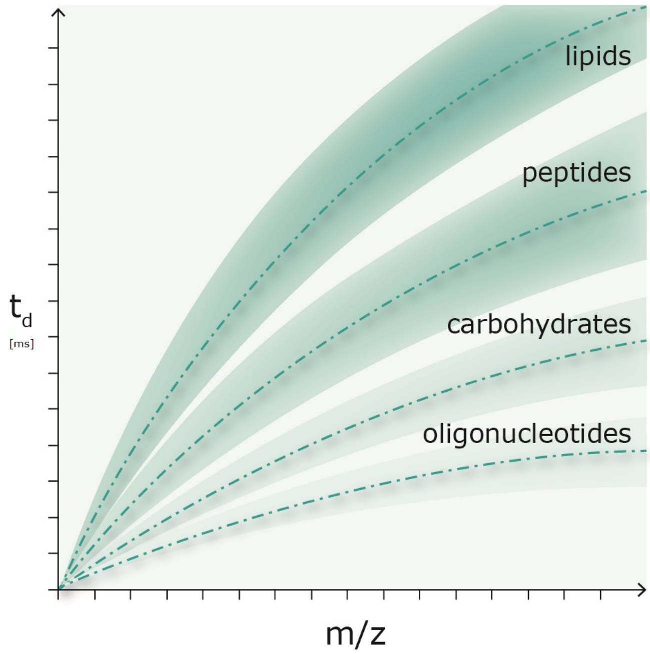


Figure 1.4.: Hypothetical ordering of biomolecular classes, according to drift time t_d. Adapted from [26].

1.3. TOF-IMS instrument configuration

The instruments used for our investigations are the Agilent 6230 TOF LC/MS [27] and Agilent 6560 Ion Mobility Q-TOF LC/MS [28]. The latter QTOF instrument contains a drift tube IMS and has been on the market since 2013. Apart from the IMS drift tube, both instruments are state-of-the art mass spectrometers with time of flight mass analyzers, while the 6560 instrument has a quadrupole and collision cell for precursor selection and fragmentation. Both instruments use the same ionization technique (electro spray ionization, ESI), with the exact same ionization source, which is important, because the first instrument was used to evaluate the limits of the detection and quantification for typical phenolic compounds and also, to assess the linear range of the measurements and transmission loss arising, from the use of the IMS functionality. An Agilent dual ESI with Jet stream technology is used (**Figure 1.5**) in the negative ionization mode, which was found to be suitable for a broad range of phenolic compounds. In an ESI source a nebulizer sprays the solution to be analyzed through a charged capillary into a chamber, with drying gas. Inside this chamber the solution droplets containing molecules are desolvated and the molecules are then softly ionized by loss or addition of a proton, and / or forming adducts with both cations and anions as Na^+ or $HCOO^-$.

The Agilent Jet stream technology also thermally focuses the electro spray, exiting the capillary to further improve transfer of ions into the MS. This is achieved through a thermal gradient between the sheath gas and the drying gas. After ionization, the ions are trapped within a square RF trapping funnel and then sent into the drift tube as

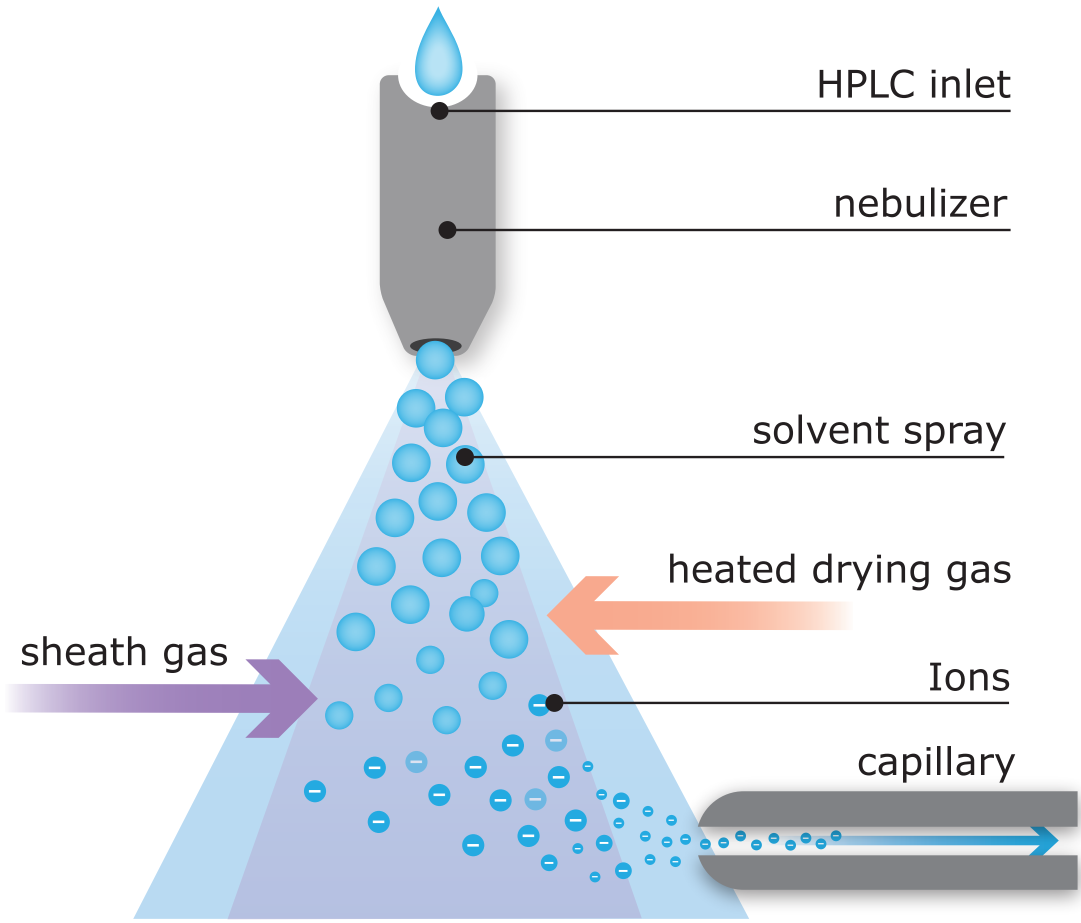


Figure 1.5.: Agilent dual ESI with Jet stream technology scheme (more information at Agilent Technologies [28]). Between the nebulizer-tip and the capillary normally a potential difference of around 4000 V is applied.

discrete packages, the time they need to reach the end of the drift tube, is determined by the extent of collisions with the neutral drift gas that retards the motion of ions inside the tube. The stacked ring-ion-guide-design of the drift tube, that can be observed in **Figure 1.6** provides a constant (DC) electrical field for the drift event.

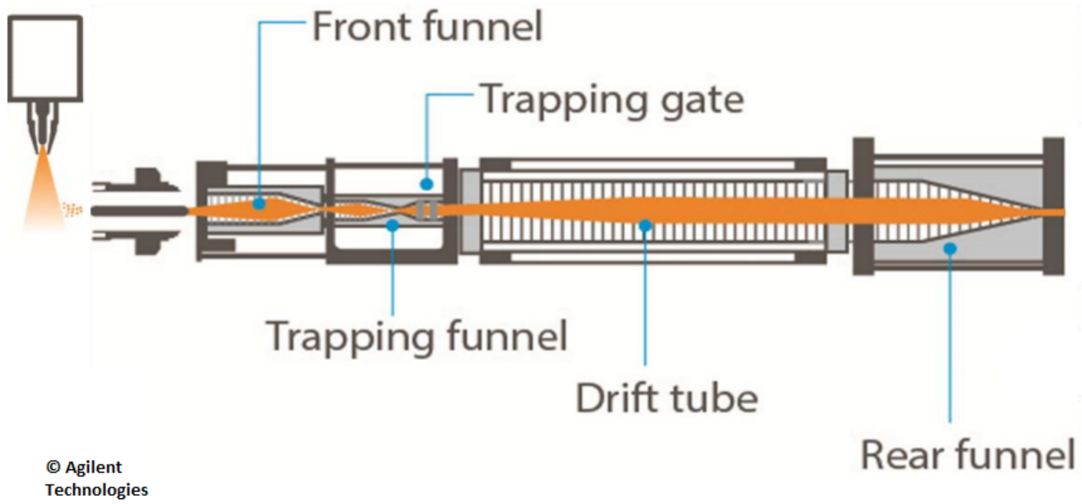


Figure 1.6.: Drift tube scheme with stacked ring ion guide design, exact length 78.2 cm.

The drift time as mentioned in the theoretical background section, is the main analytical parameter and can then be used to obtain the t_d versus $1/\Delta V$ plot, used to calculate the CCS value for a given ion with either a stepped-field, or single-field calibration method. Following the drift separation, packages of ions are then guided further into the quadrupole and accelerated into the time of flight analyzer, where accurate high resolution mass spectra are collected. The combination of the two separation principles (shape-to-charge and mass-to-charge) with a high performance liquid chromatography system therefore, provides a very high level of separation possibilities. The detailed methods used with each system, will be explained in the experimental section.

1.3.1. Resolution

Ion mobility spectrometry can be considered, to have characteristics of both chromatography and mass spectrometry. However, the resolution of drift-tube ion mobility is much lower than for mass spectrometry, as collisions (between analyte ions and neutral drift gas molecules in a low-field setting) are required.

"[. . .],IMS resolution is independent of the ion being separated and is directly proportional to the square root of the potential across the ion drift region (EL) and inversely proportional to the square root of the drift gas temperature." [29]

As the temperature and pressure in the case of the used instrument are kept constant, resolution then depends principally on the drift tube length L (78.2 cm) and the field strength over the drift region $E = {}^{V}/_{cm}$ which can be calculated via equation (1.5) , where t_d is the drift time, Q is the charge state of the ion and T is the absolute temperature [29].

Achieving higher resolution by applying higher field strength, has its limits due to the potential for arcing in the drift-tube, while very high field strengths lead to non-linear behavior, which makes determination of CCS values difficult. Conversely, low field strength, will effect the measurement as diffusion processes become very significant, which leads to peak broadening, loss of signal strength, intensity and resolution.

$$R = \frac{t}{\Delta t} = \sqrt{\frac{LEQ}{16kT \ln 2}} \tag{1.5}$$

1.3.2. Separation

As one of the main goals of adding IMS into LC-MS methods is further separation of complex mixtures of compounds; the separation potential of this combination is of interest. An important parameter of separation is the concept of peak capacity of a system. The coupling of LC-IMS-MS provides an already good capacity from the LC and MS part, but is additionally enhanced by the addition of the orthogonal ion mobility separation. Following equation (1.6), an eight fold increase of peak capacity should be achievable, in comparison to a LC-MS system alone [30].

$$\text{Peak Capacity} = IM_{\text{Resolution}} \times MS_{\text{Resolution}} \times \text{Orthogonality} \tag{1.6}$$

2. Experimental

2.1. Reagents and materials

Wine samples were purchased at the local supermarket. Three red wines from different heritage were used, two from Austria, one from Australia for the comparison analysis. The wines used were: Shiraz Heritage Release South Eastern Australia 2013; by Wolf Blass, Cuvée Tradition Blaufränkisch, Zweigelt and Merlot 2014 by Anton Iby Emotion Wine and Flat Lake Limitation Blaufränkisch-Zweigelt 2014; by Leo Hillinger. The wine used for the repeatability study, was Blauer Zweigelt Reserve Burgenland 2013, by Lenz Moser.

All the chemicals used for the mobile phase and buffer preparations where high grade MS chemicals purchased, from Sigma-Aldrich or Fluka (see Appendix). The mobile phases were filtered through membrane filters.

2.2. Sample preparation

The same procedure of preparation was used for the different methods to ensure comparability and was adapted from the method of Jaitz [15]. The freshly opened wines were filtered, (Iso-DiscTM, N-4-4, Nylon, 4 mm × 0.45 µm, Supelco, Bellefonte, PA, U. S.) and diluted 1:10 with 10 mmol L^{-1} ammonium formate buffer (with a pH of 3.75 containing 10 % v/v methanol) to a final volume of 1 mL. A multi-compound standard, to assess retention times and mass spectra for some expected compounds in wine, was prepared.

A stock concentration of 5 $\mu\text{mol L}^{-1}$ for each substance was prepared in a 10 mmol L^{-1} ammonium formate buffer (with a pH of 3.75 containing 10 % v/v methanol) and diluted to a final concentration of 25 $\mu\text{mol L}^{-1}$, with 250 $\mu\text{mol L}^{-1}$ of internal standard (α,α,α-Trifluoro-m-toluic acid). **Table 2.1** gives an overview over the used standard substances.

Table 2.1.: List of used standard substances and the internal standard.

Compound	Sum formula	MW [$g\,mol^{-1}$]	Supplier
p-Coumaric acid	$C_9H_8O_3$	164.16	SIGMA C9008
Gallic acid · H_2O	$C_7H_6O_5$	188.13	ROTH 7300.1
Naringenin	$C_{15}H_{12}O_5$	272.25	SIGMA W530098
Kaempherol	$C_{15}H_{10}O_6$	286.24	SIGMA 60010
Catechin	$C_{15}H_{14}O_6$	290.27	FLUKA C1788
Epicatechin	$C_{15}H_{14}O_6$	290.27	SIGMA E1753
Quercetin	$C_{15}H_{10}O_7$	302.24	SIGMA Q4951
Myricetin	$C_{15}H_{10}O_8$	318.24	SIGMA M6760
Trifluoro-*m*-toluic acid	$C_8H_5O_2F_3$	190.12	SIGMA 188344

2.3. LC-IM-TOFMS method

An Agilent 1290 Infinity II LC system was coupled to an Agilent 6560 IMS-QTOF mass spectrometer, equipped with an Agilent G1607A dual Jetstream coaxial ESI source and an upgraded ion mobility alternate gas kit with electronic drift gas pressure control, keeping the gas pressure inside the drift tube in between 3.954 Torr and 3.955 Torr.

Chromatographic separations were performed at a temperature of 40 °C, using a Zorbax C18 SB Rapid Resolution column (2.1 × 50 mm) using a conventional reversed-phase mobile phase gradient.

Eluent A contained 0.1 % v/v formic acid in water, and Eluent B contained 0.1 % v/v formic acid in acetonitrile. Using a solvent flow rate of 350 $\mu L\,min^{-1}$, an initial composition of 99 % A was held for 2 minutes, followed by a compositional gradient from 1 % to 50 % B in 2-15 minutes, then increasing to 70 % from 15-16 minutes. This composition was held for 1 minute prior to returning to 1 % B and holding for 2 minutes (total run time of 20 minutes). The injection volume was 5 µL.

All analyses were performed in the negative ionization mode. For all measurements, nitrogen was used as drying gas at a temperature of 360 °C, a sheath gas temperature of 150 °C and a sheath gas flow rate of 13 $L\,min^{-1}$, to achieve the before mentioned thermal gradient. The nebulizer gas pressure was 20 psi, the MS capillary voltage was −4000 V, the nozzle voltage −2000 V and the fragmentor was set to −275 V. The scanning mass range was from 100 m/z to 1700 m/z with a TOF acquisition rate of 3 spectra × s^{-1}. The mass spectrometer was calibrated each day, using the supplied calibrant masses of the manufacturer prior to the commencement of measurements. The secondary sprayer was used to infuse solution containing reference calibrant masses constantly during the analysis.

2.4. LC-IM-QTOFMS method

When operating in the IMS-QTOF mode, the square RF trapping funnel located in front of the drift tube is utilized to sequentially trap and release packages of ions from the stream of ions entering via the ESI interface [31].

For these experiments, the instrument was tuned to optimize the transmission of fragile ions (50-250 m/z) in the 2 GHz extended dynamic range mode.

The trapping funnel was operated with a trapping time of 40 000 µs and released packages of ions every 60 ms (i. e. no multiplexing was employed) with a gate width of 150 µs set within the software.

The drift tube was operated with an absolute entrance voltage of ±700 V and an exit voltage of ±250 V, with a drift tube pressure set to 3.95 Torr and temperature of 30 °C, using high purity nitrogen as the collision gas. The acquisition settings were adjusted to yield 2.8 frames per second, corresponding to approximately 5 ion mobility transients per frame, and approximately 501 TOF transients per IM transient. The collection of MS/MS spectra in the IMS-QTOF mode was facilitated by using the "alternating frames" setting, whereby the energy in the collision cell (located post-drift tube) was set to alternate between −40 V and 0 V between frames for the entire duration of the measurement.

High-purity nitrogen was used as the collision gas. In this mode, the number of TOF transients per frame is effectively halved, as 50 % of the duty time is dedicated to the high collision energy frames.

2.5. Data handling

All optimization and evaluation calculations were performed using Microsoft Excel. MS and IMS data analysis and identification of compounds were performed using Mass Hunter Workstation Version B.07.00, from which Qualitative Analysis and Quantitative Analysis as well as Profinder B.06.00 were used. In addition, Mass Hunter IM-MS Browser Version B.07.01 was used to handle the LC-IM-MS data and Mass Hunter Profiler B.07.00 was used to align features across two groups of samples. For plotting of data, analyses were exported as .csv files and visualized with Microsoft Excel for better comprehension. Blanks were measured every other analysis and considered in data evaluation, especially for feature annotation.

3. Results and discussion

3.1. Quantitative aspects of LC-TOF approach

As TOF instrumentation has a limited linear working range compared to a triple Quad or similar MS analyzers, the linearity of the detector response and limit of detection were determined (**Table 3.1**) using an Agilent 6230 TOF LC/MS instrument equipped with the same ion source running under the same chromatographic conditions.

The acquired data were used, to give an indication of the expected sensitivity and linearity for further work, which was undertaken with the Agilent 6560 Ion Mobility Q-TOF LC/MS instrument, which has a longer flight tube and some differences in the ion optics in addition to the ion mobility drift tube. The repeatability (**Section** 3.4)

Table 3.1.: Limits of detection (LOD) and quantification (LOQ) of the standard substances measured with the Agilent 6230 TOF LC/MS instrument. Calculated according to the Eurachem guidelines [32].

Compound	LOD [$\mu g\,L^{-1}$]	LOD [$\mu mol\,L^{-1}$]	LOQ [$\mu g\,L^{-1}$]	LOQ [$\mu mol\,L^{-1}$]
p-Coumaric acid	19.4	65	120	400
Gallic acid	8.8	29	47	160
Naringenin	18	60	66	220
Kaempherol	37	120	120	430
Catechin	18	58	60	200
Epicatechin	21	71	73	250
Quercetin	22	73	73	240
Myricetin	11	38	36	120

and robustness of the chromatographic separation was satisfactory (**Fig. 3.1**) and thus the method was ready to be moved to the new HPLC system of the Agilent 6560 Ion Mobility Q-TOF LC/MS instrument.

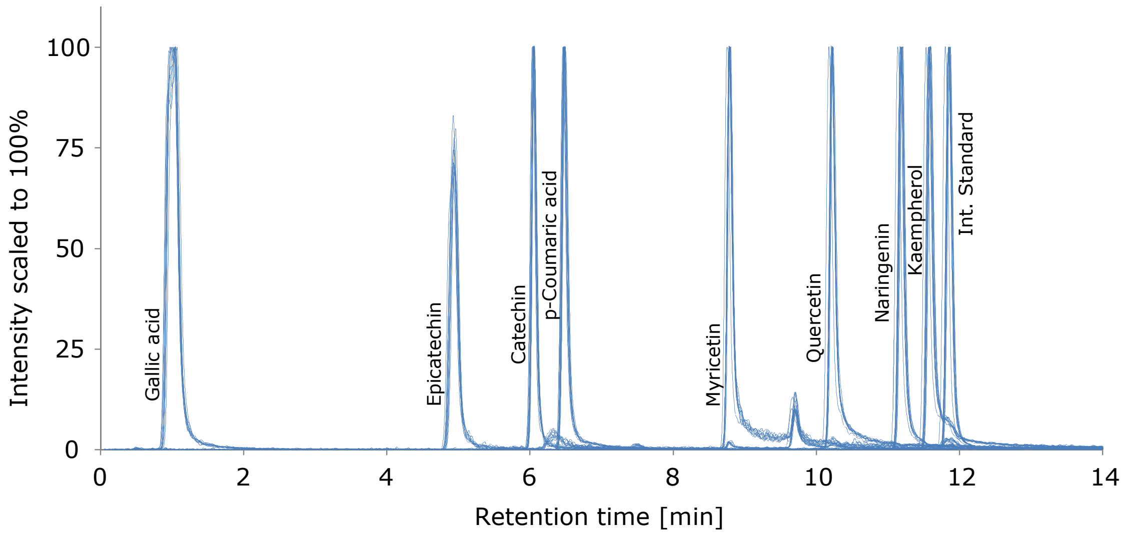


Figure 3.1.: The extracted ion chromatograms (EIC) of all standards and the internal standard from 10 measurements on the Agilent 6230 TOF LC/MS instrument overlaid, show excellent repeatability and good separation. The Myricetin standard shows some impurities at about 6 min and 10 min. All peaks were scaled to the Internal Standard as 100 %.

3.2. Transmission

One thing to consider with a drift region between the ion source and the rest of the mass spectrometer, is the impact on ion transmission. Comparison was done with the IMS turned on to a TOF-only method, the results can be observed in **Fig. 3.2**. Basically, there will always be a loss of intensity with more way for the ions to cover, however, the method used in this example can be further improved considering, that through the used trapping time of 40 ms and a package release time of 60 ms $1/3$ of the usable time for trapping, was given up.

Further there will be an option within the software, called multi plexing, where ion packages are injected more frequently in a pseudo-random sequence allowing packages of "fast" ions to overtake "slow" ions from the previous package. The software can deconvolute this pattern and reconstruct the IMS separation. Less trapping time is beneficial as space-charging effects (leading to transmission losses) can be minimized.

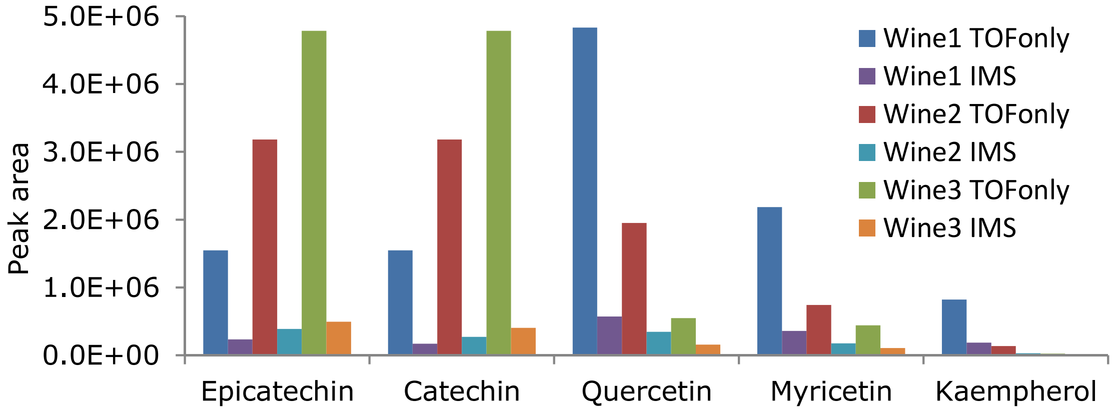


Figure 3.2.: Abundance (chromatographic peak area) comparison of five substances extracted from the wine samples, retention times and m/z agreeing within their certainty with the standard substances. The transmission loss in IM mode can be observed by comparing the columns next to each other and is ≈ 85%.

3.3. CCS measurements of phenol standards

With ion mobility as part of the workflow, benchmarking of the CCS precision was undertaken. Comparison of the CCS values acquired through a stepped-field method and values acquired with a single-field method shows, that the relative standard deviation (RSD) lies $< 1\%$. Some of the standard substances where only measured with the stepped-field method, because they are not abundant enough in wine (Naringenin) or elute from the chromatographic system before 2 minutes (Gallic acid). To be sure that, only reliable features were picked up, the feature extraction window was set to 2 minute to 16 minutes.

To assess the CCS value of a flavonoid glucoside in addition to the standards at hand, a Rutin standard was measured with the stepped filed method and the results provided information which values could be expected for this substance class. The stepped-field measurement where executed in an intra- and inter-day manner. For the intra-day study on one day three measurements in a row were executed and this was repeated over three days, to gain information on the repeatability of the measurements. All results are compiled in **Table** 3.2 and the data set shows, that the CCS precision is not much different between the two approaches (**Fig.** 3.3). Trueness of values, however, can not be assessed due to the fact, that there are no sources for the true values yet.

Table 3.2.: Comparison of the CCS values, acquired with the stepped-field approach to the values, acquired with the single-field calibration method.

Compound	single-field [$\AA^2$]	stepped-field$_{\text{(intra day)}}$ [$\AA^2$]	stepped-field$_{\text{(inter day)}}$ [$\AA^2$]
p-Coumaric acid	-	135.4 ±0.53	135.2 ±0.53
		134.9 ±0.32	
		135.3 ±0.20	
Gallic acid	-	128.7 ±0.23	128.7 ±0.25
		128.6 ±0.23	
		128.8 ±0.31	
Naringenin	-	168.6 ±0.20	168.6 ±0.24
		168.5 ±0.20	
		168.6 ±0.31	
Kaempherol	166.2 ±1.23	166.7 ±0.46	166.8 ±0.32
		166.7 ±0.23	
		166.9 ±0.20	
Catechin	161.0 ±0.60	161.0 ±0.72	160.9 ±0.50
		160.7 ±0.23	
		161.1 ±0.23	
Epicatechin	161.1 ±0.52	160.5 ±0.64	160.5 ±0.43
		160.3 ±0.12	
		160.5 ±0.40	
Quercetin	168.5 ±0.47	169.4 ±0.42	169.4 ±0.41
		169.3 ±0.31	
		169.6 ±0.20	
Myricetin	170.9 ±0.36	172.2 ±0.31	172.3 ±0.47
		172.1 ±0.31	
		172.6 ±0.12	
Rutin	-	238.1 ±0.12	238.1 ±0.47
		237.8 ±0.31	
		238.3 ±0.35	

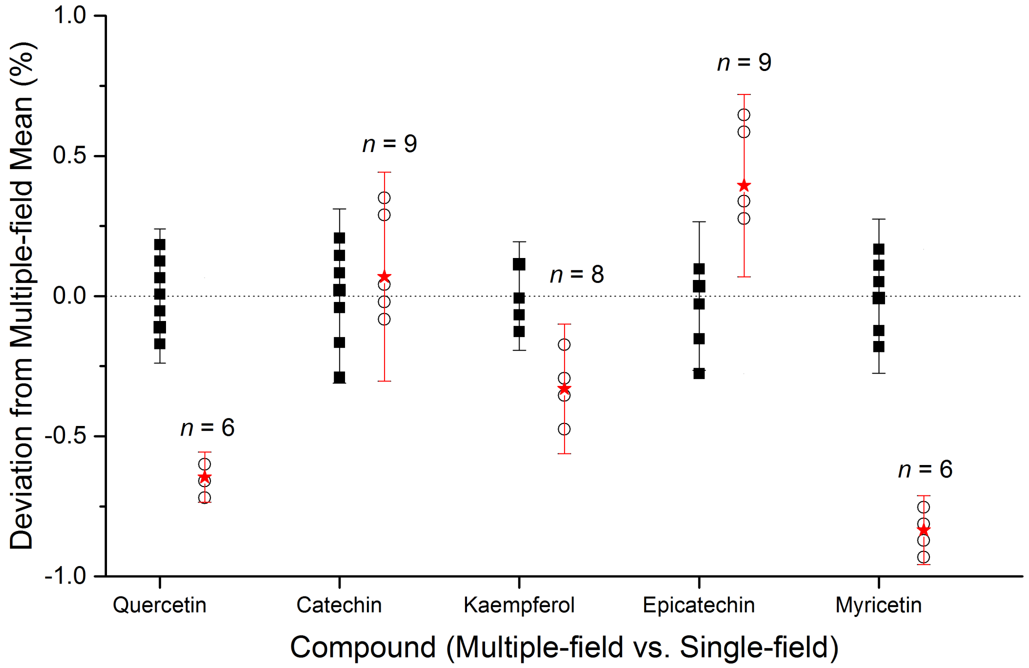


Figure 3.3.: CCS comparison between the stepped-field (■) and the single-field (○) approach. The values with the higher deviation from the the mean are determined with the single-field approach, n indicates the number of reliable annotated features from wine and standard measurements.

3.4. Repeatability

To ensure that the retention time, m/z and t_d are repeatable, consecutive measurements of the same wine (mentioned in the experimental section) where undertaken. The **Table 3.3** shows the extracted masses of the substances from **Table 1.1** with their values and standard deviation. Furthermore, the base peak chromatograms (BPC) of the consecutive runs, were overlaid to show the repeatability of the results (**Fig. 3.4**).

Table 3.3.: Suggested substance for the extracted masses from the 6 repeatability measurements, aligned to the substance by retention time, drift time and m/z showing no significant difference to standard substances, or thoughtful investigation in **Section 3.7**. Note that for the castavinol example no decision, on which exact isomers are separated in the drift dimension, was made. * Indicates a putative identification.

Compound	Retention time [min]	Drift time [ms]	CCS [$Å^2$]	$m/z_{measured}$	$[M\text{-}H]^-_{predicted}$	$mass_{div}$ [ppm]
Kaempherol	10.11 ±0.004	19.96 ±0.014	166.2 ±0.12	285.0399 ±0.0004	285.0405	2.2
Epicatechin	4.182 ±0.002	19.34 ±0.004	160.9 ±0.04	289.0705 ±0.0004	289.0718	4.5
Catechin	5.184 ±0.003	19.34 ±0.009	160.9 ±0.08	289.0711 ±0.0004	289.0718	2.3
* Caftaric acid *a*	3.310 ±0.007	19.83 ±0.006	164.5 ±0.04	311.0403 ±0.0004	311.0409	1.9
* Caftaric acid *b*	3.311 ±0.007	21.66 ±0.009	179.6 ±0.09	311.0401 ±0.0004	311.0409	2.6
* Miquelianin	6.716 ±0.003	25.50 ±0.022	208.3 ±0.18	477.0662 ±0.0004	477.0675	2.8
* Castavinol *a*	6.120 ±0.051	27.79 ±0.092	225.9 ±0.75	565.1536 ±0.0007	565.1557	3.7
* Castavinol *b*	6.127 ±0.046	28.63 ±0.029	232.8 ±0.25	565.1541 ±0.0012	565.1557	3.0

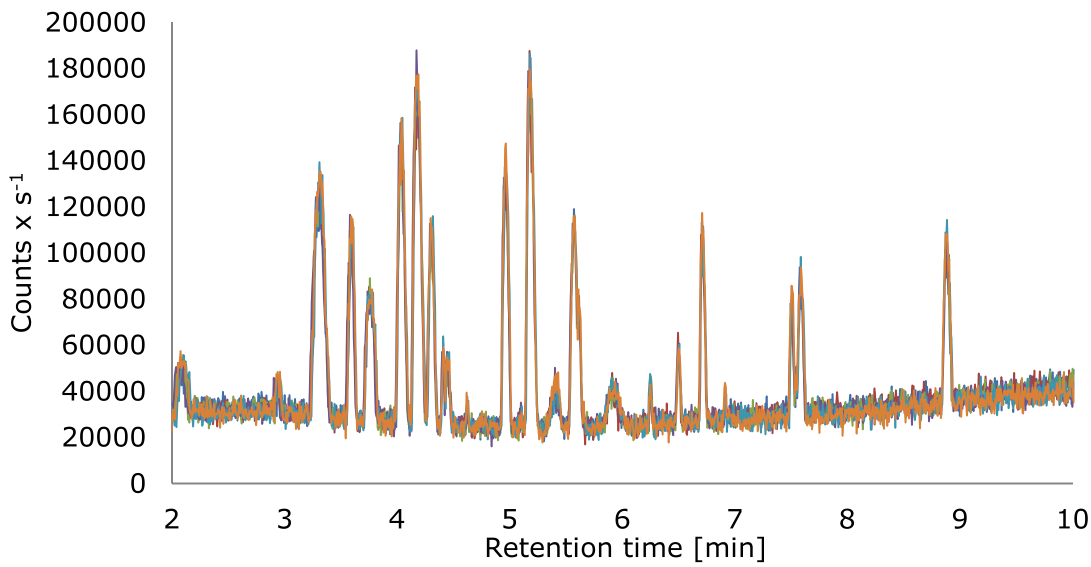


Figure 3.4.: Six overlaid BPCs of the same wine measurement, to show repeatability of the analytic approach.

3.5. LC-IM-TOF measurements

The three wine varieties were measured and feature lists extracted with Mass Hunter Profiler B.07.00. Features where then filtered according to abundance ≥ 1000 ion volume, assigned charge state -1 or -2 and Q-Score ≥ 80. This data set was used, to create a comparison (**Fig. 3.5**) between the different varieties and the TOF only approach (**Fig. 3.6**). The "unique" features must be seen as features that are not found in high enough abundance, or are not aligned well enough according to the filter settings applied by the user. Without a recursive extraction process, it is only possible to manually assess if all "unique" compounds are actually present in the other samples. Not picking up a feature in ion mobility mode in comparison to TOF only mode mostly means, that the abundance for an isotope peak or drift time peak has dropped to low for the algorithm to assign a charge state, or a drift time and the feature is then filtered out, because of the set options.

This is an important thing to consider, as in TOF only mode a lot of features get charge states even though they are, a closer look taken, not really above the chromatographic noise level. Making the split between confidence and feature number is one thing to be aware of, in general for a certain workflow.

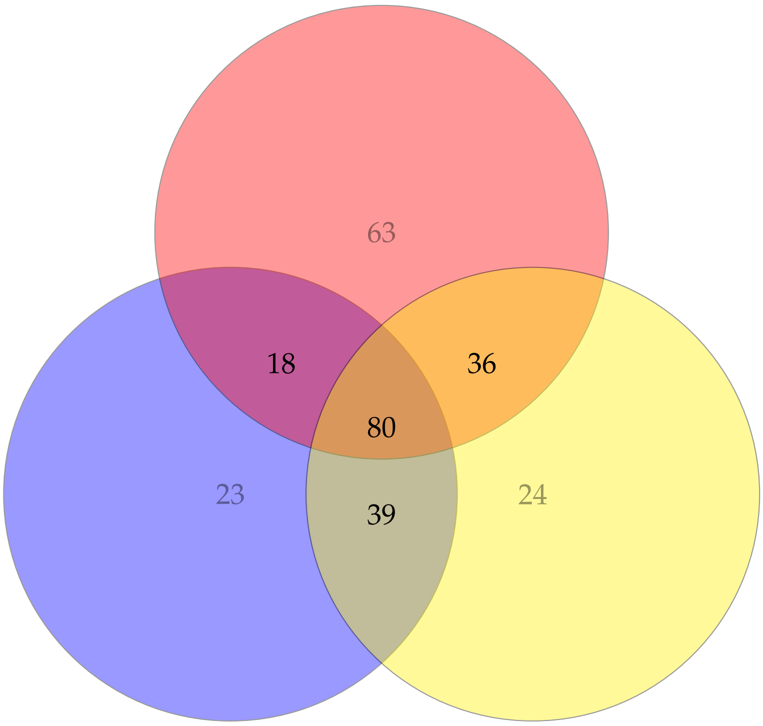


Figure 3.5.: Venn diagram showing the feature distribution over the different wine varieties in IM mode, Shiraz (red), Blaufränkisch-Zweigelt-Merlot (blue) and Blaufränkisch-Zweigelt (yellow).

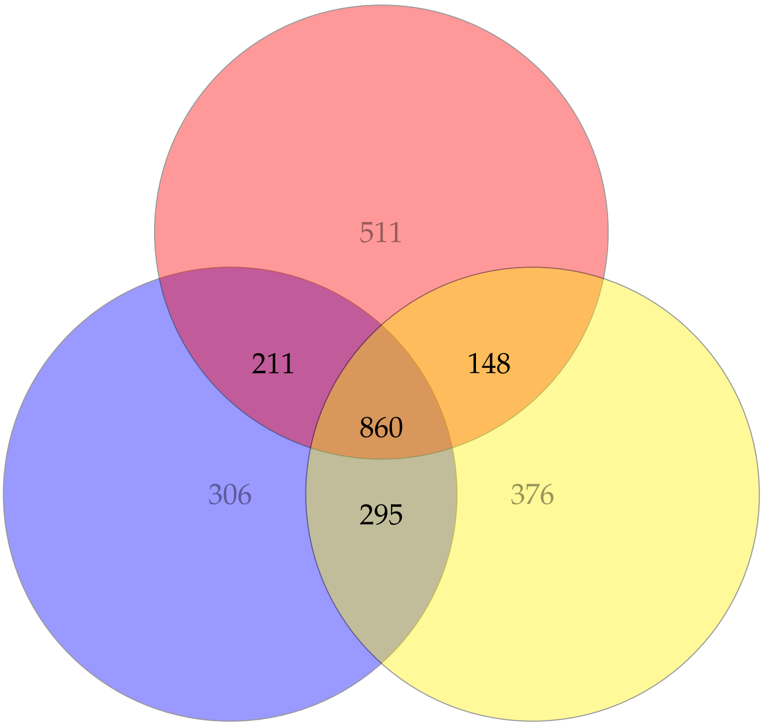


Figure 3.6.: Venn diagram showing the feature distribution over the different wine varieties in TOF only mode, Shiraz (red), Blaufränkisch-Zweigelt-Merlot (blue) and Blaufränkisch-Zweigelt (yellow).

3.6. LC-IM-QTOF

The alternating frames mode enables the possibility to measure fragmentation spectra of ions coming out of the drift tube, at a certain moment every other recorded frame. Using these additional time locked fragmentation spectra, fragments detected at the same drift time, can confirm assumptions made for the structural properties of annotated features. A short example (**Fig.** 3.7) will be given in this section and fragmentation spectra will be used in **Section** 3.7 to help with feature identification.

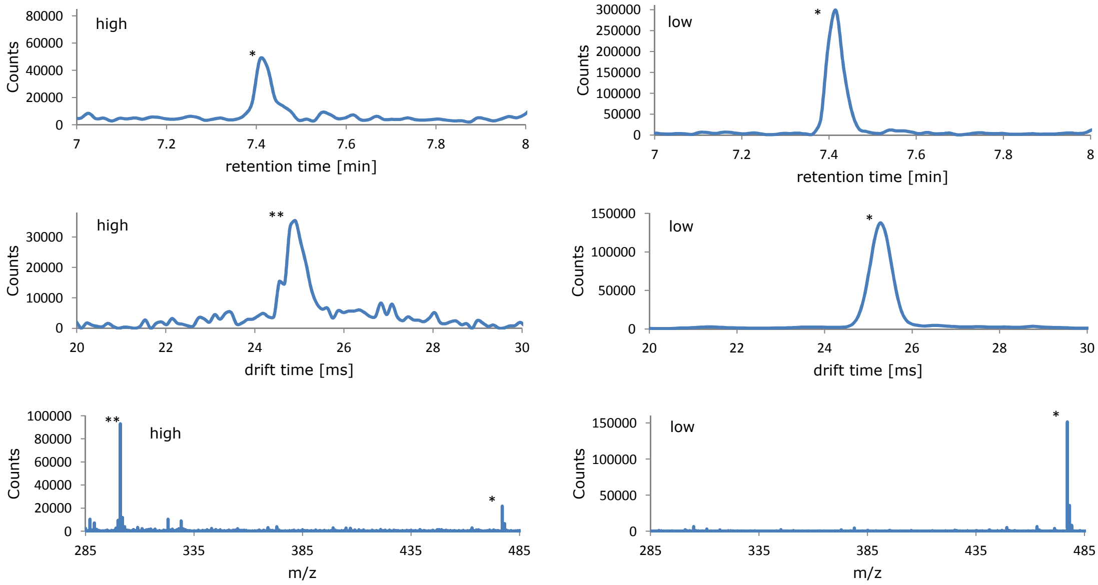


Figure 3.7.: A full comparison of high and low fragmentation frame spectra, from the mass 477.0675 m/z in a mass window from 476.9981 to 480.4988 m/z and a drift time window of 12.03 to 33.33 ms, extracted from the Shiraz sample. The values of the retention time and drift time of the precursor and the fragment as well as the mass spectra agree within their certainty. Showing the fragmentation behavior, gives valuable information for feature identification.

3.7. Qualitative examples

Through the combined usage of retention time accuracy, IMS data and alternating frames fragmentation data with high resolution, putative identification of features receives additional backup. Detailed examples for the isobaric pair epicatechin/catechin and kaempferol are shown using information from the analysis of standards as well as for some unknown compounds found in wine. It should be noted that, due to fragmentation taking place after the drift tube, fragments are going to have slightly shifted drift times.

3.7.1. Kaempherol

With the information of **Table 3.3** it is easy to compare the values shown in the spectra collection in **Fig. 3.9**, that represent the overlaid chromatograms, drift spectra and mass spectra from low and high fragmentation frames in alternating frames mode, as well as the EIC of the kaempherol standard.

The drift time and EICs of the fragments, show no significant difference (10.93 min ± 0.034 and 19.74 ms ± 0.20) with the times in the low fragmentation frame and in the non alternating frames mode. The example shows, that the values of the product ions agree with the drift time and the retention time, well in this particular case. Only the low abundance in the alternating frames mode was an issue, in being able to extract all fragment spectra, therefore only tow spectra could be shown, indicating that MS/MS settings need to be optimized to make better use of the IM-QTOF mode. Furthermore, manual interrogation of features is very time-consuming without an LC-MS and LC-MS/MS library.

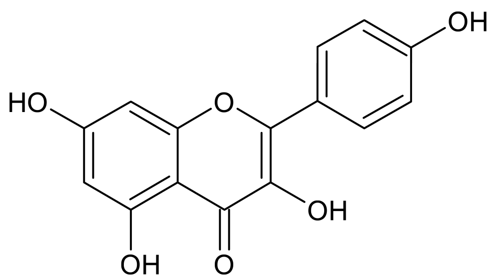


Figure 3.8.: Chemical structure of Kaempherol, sumformula $C_{15}H_{10}O_6$, exact mass of the $[M-H]^-$ ion 285.0405 m/z.

Table 3.4.: These extracted ions are plotted in the **Fig. 3.9** and are used for the putative identification of kaempherol.

Kaempherol	spectrum	fragmentation frame	drift range [ms]	mass range [m/z]	retention time range [min]	sample
1	drift	no fragmentation	-	285.0271-285.0505	10.872-10.956	shiraz
2	drift	low	-	284.9059-285.4194	10.820-11.106	shiraz
3	drift	high	-	159.0197-159.0850	10.820-11.106	shiraz
4	drift	low	-	285.0225-285.1042	10.850-10.946	shiraz
5	drift	high		130.9356-131.0463	10.850-10.946	shiraz
1	EIC	no fragmentation	19.37-20.34	285.0224-287.1030	-	shiraz
2	EIC	low	19.37-20.46	285.0276-287.0965	-	shiraz
3	EIC	high	-	159.0365-159.0649	-	shiraz
4	EIC	low	19.37-20.46	285.0267-287.0838	-	shiraz
5	EIC	high	19.37-20.46	285.0267-287.0838	-	shiraz
1	mass	low	19.37-20.46	-	10.820-11.106	shiraz
2	mass	high	19.37-20.46	-	10.820-11.106	shiraz
3	mass	no fragmentation	17.57-22.38	-	10.872-10.956	shiraz
4	mass	low	18.65-20.58	-	10.850-10.946	shiraz
5	mass	high	18.89-20.82	-	10.850-10.946	shiraz

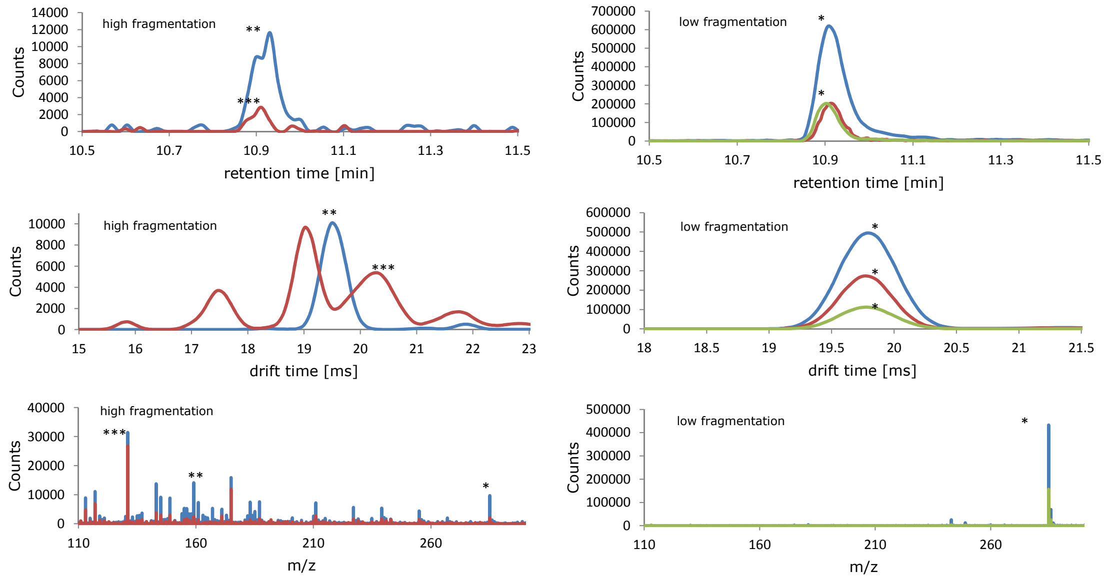


Figure 3.9.: In this example, the values of retention time and drift time of fragments and precursor ion of kaempherol agree within their certainty. There was no significant difference of drift time, retention time and mass spectra between kaempherol and its standard. Using the algorithm of the Mass Hunter Workstation Version B.07.00, a sum formula was assigned to the ion, too. The plotted ions with their respective extraction windows can be observed in **Table 3.4**.

3.7.2. Epicatechin/Catechin

One of the questions concerning separation in the drift dimension is, how different the structures of molecules must be, to have a chance to separate them. In this example two stereo-isomers were used to assess their behavior in the drift tube. They do not separate at all and it looks like the analytic approach is not able to achieve any kind of separation for such small differences seen for some phenolic compounds.

As the two compounds are separated in the chromatography so well, it is critical, that HPLC is a major part of the analytical approach. Again in this example the retention times, drift times and m/z were controlled with the standards and backed up with the algorithm of the Mass Hunter Workstation Version B.07.00.

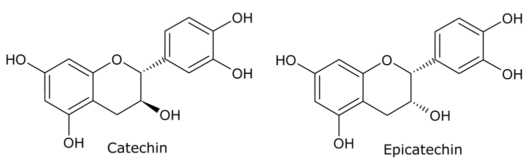


Figure 3.10.: Chemical structure of the isobaric pair catechin/epicatechin, sumformula $C_{15}H_{14}O_6$, exact mass of the $[M-H]^-$ ion 289.0718 m/z.

Table 3.5.: These extracted ions are plotted in the **Fig. 3.11** and used for the putative identification of catechin/epicatechin.

Epicatechin/catechin	Spectrum	fragmentation frame	drift range [ms]	mass range [m/z]	retention time range [min]	sample
1	drift	no fragmentation	-	287.7237-289.9905	5.148-5.244	shiraz
2	drift	no fragmentation	-	287.7232-289.9901	5.973-6.040	shiraz
3	drift	low	-	273.7597-313.9993	5.148-5.226	standard
4	drift	high	-	158.9883-159.1278	5.148-5.226	standard
5	drift	low	-	288.7856-289.6259	5.963-6.059	standard
6	drift	high	-	159.0198-159.0983	5.963-6.059	standard
7	drift	low	-	288.9727-289.4251	5.127-5.257	shiraz
8	drift	high	-	123.0346-123.0576	5.127-5.257	shiraz
9	drift	high	-	125.0087-125.0512	5.127-5.257	shiraz
10	drift	low	-	289.0438-289.1025	5.977-6.054	shiraz
11	drift	high	-	123.0347-123.0577	5.977-6.054	shiraz
12	drift	high	-	125.0087-125.0590	5.977-6.054	shiraz
1	EIC	low	18.77-19.74	289.0554-291.1093	-	standard
2	EIC	high	-	159.0375-159.0631	-	standard
3	EIC	no fragmentation	18.65-19.74	289.0560-291.1040	-	shiraz
4	EIC	low	18.65-19.74	289.0544-291.1201	-	shiraz
5	EIC	high	18.65-19.74	289.0544-291.1201	-	shiraz
6	EIC	high	18.77-19.86	289.0544-291.1083	-	shiraz
7	EIC	low	18.77-19.86	289.0544-291.1083	-	shiraz
8	EIC	low	18.65-19.86	289.0544-291.1024	-	blaufränkisch-zweigelt-merlot
9	EIC	high	18.65-19.86	289.0544-291.1024	-	blaufränkisch-zweigelt-merlot
10	EIC	low	18.65-19.86	289.0542-291.1258	-	blaufränkisch-zweigelt
11	EIC	high	18.65-19.86	289.0542-291.1258	-	blaufränkisch-zweigelt
1	mass	low	18.65-19.74	-	5.148-5.226	standard
2	mass	no fragmentation	17.45-21.06	-	5.148-5.244	shiraz
3	mass	low	18.53-20.10	-	5.127-5.257	shiraz
4	mass	high	18.53-20.10	-	5.127-5.257	shiraz
5	mass	low	18.53-20.10	-	5.977-6.054	shiraz
6	mass	high	18.53-20.10	-	5.977-6.054	shiraz

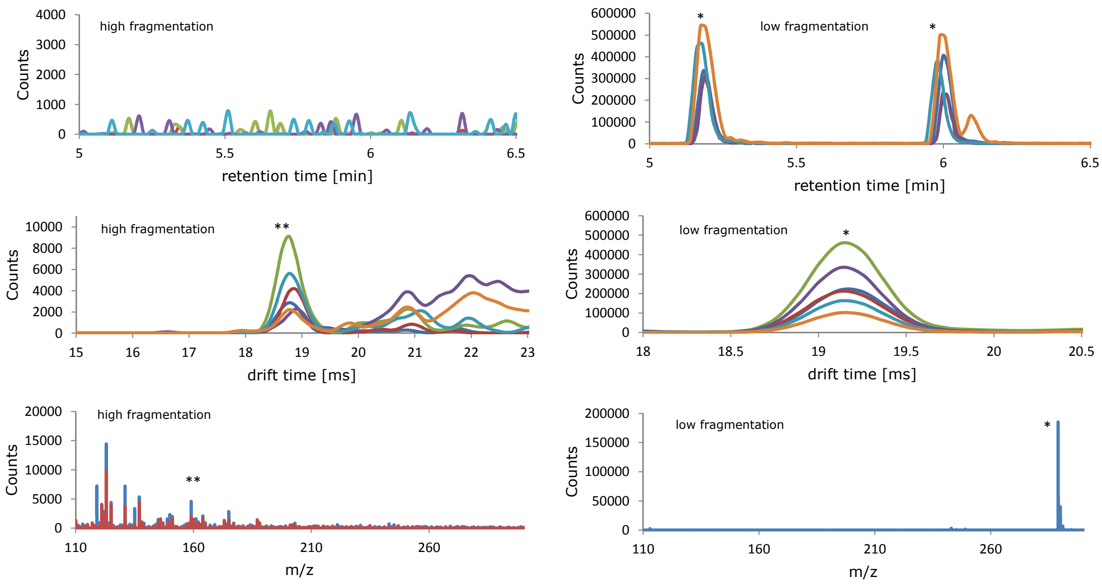


Figure 3.11.: Epicatechin/catechin is an example, where there is a chromatographic separation of the two isobars (see also **Fig. 3.1**), but in the drift spectra all extractions show the same drift time. The plotted ions with their respective extraction windows can be observed in **Table 3.5**.

3.7.3. Miquelianin

In the case of the tentatively identified quercetin-(3)-O-glucuronide, the abundance of the substance is not the problem, but the consistency of the retention time in the three wine samples is out of the normally encountered range. However, the drift times of the precursors and fragments do not significantly differ. Considering the retention time windows used for recursive extractions, one of the features could get lost, when relaying only on retention time and mass.

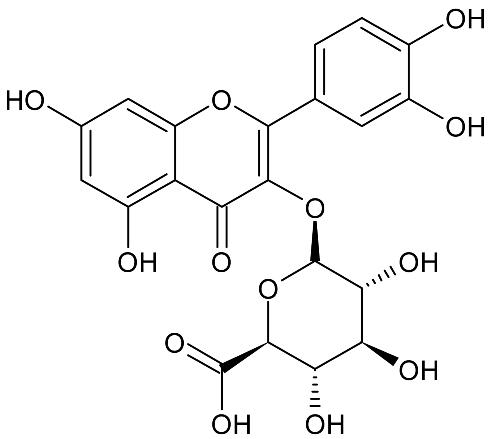


Figure 3.12.: Chemical structure of the quercetin-(3)-O-glucuronide miquelianin, sumformula $C_{21}H_{18}O_{13}$, exact mass of the $[M-H]^-$ ion 477.0675 m/z.

Table 3.6.: These extracted ions are plotted in the **Fig. 3.13** and are used for the tentative identification of miquelianin.

Miquelianin	Spectrum	fragmentation frame	drift range [ms]	mass range [m/z]	retention time range [min]	sample
1	drift	low	-	475.5541-483.9703	7.364-7.546	shiraz
2	drift	high	-	300.7571-303.4357	7.381-7.460	shiraz
3	drift	low	-	477.0084-477.1518	7.347-7.425	blaufränkisch-zweigelt-merlot
4	drift	low	-	477.0198-477.1406	7.393-7.454	blaufränkisch-zweigelt
5	drift	high	-	300.9179-301.1637	7.347-7.425	blaufränkisch-zweigelt-merlot
6	drift	high	-	301.0195-301.0494	7.393-7.454	blaufränkisch-zweigelt
1	EIC	low	-	476.9981-480.4988	-	shiraz
2	EIC	high	-	476.9981-480.4988	-	shiraz
3	EIC	low	24.67-25.99	477.0418-479.1044	-	blaufränkisch-zweigelt-merlot
4	EIC	high	24.79-26.23	477.0490-478.1138	-	blaufränkisch-zweigelt
5	EIC	high	24.67-25.99	477.0418-479.1044	-	blaufränkisch-zweigelt-merlot
6	EIC	low	24.79-26.23	477.0490-478.1138	-	blaufränkisch-zweigelt
1	mass	low	12.03-33.33	-	7.381-7.460	shiraz
2	mass	high	12.03-33.33	-	7.381-7.460	shiraz
3	mass	low	22.98-27.56	-	7.347-7.425	blaufränkisch-zweigelt-merlot
4	mass	low	23.83-27.20	-	7.393-7.454	blaufränkisch-zweigelt
5	mass	high	22.98-27.56	-	7.347-7.425	blaufränkisch-zweigelt-merlot
6	mass	high	23.83-27.20	-	7.393-7.454	blaufränkisch-zweigelt

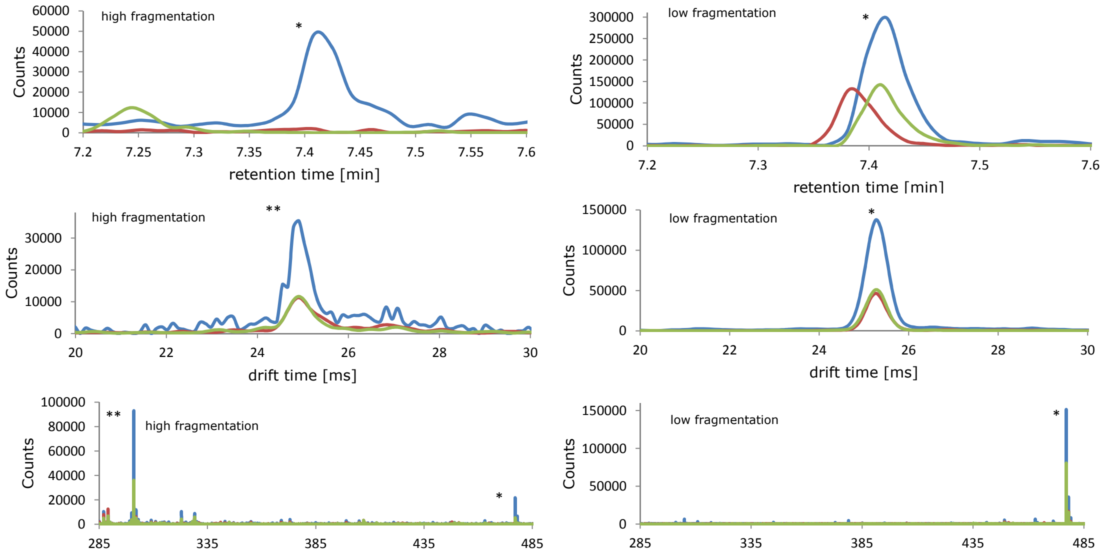


Figure 3.13.: Miquelianin is proposed as structure for this spectra composition, because of values of the masses agreeing within their certainty and forming of a drift locked fragment at the mass of the $[M-H]^-$ ion of quercetin at 301.0354, as well as backed up from the algorithm of the Mass Hunter Workstation Version B.07.00 concerning the sumformula. The plotted ions with their respective extraction windows can be observed in **Table 3.6**.

3.7.4. Caftaric acid

Caftaric acid was chosen to investigate, if the two isomers (cis/trans) would separate in the drift domain. The extracted spectra show, that in this case the chromatography alone is not able to achieve base line separation, whereas the two isomers are clearly separated in the drift domain. The drift spectra of the fragment ions are very noisy probably, because of low abundance and overlapping of the two fragments tartaric acid and caffeic acid for each isomer. The two fragments can be observed in the low and high fragmentation frames. The ion mobility difference for cis/trans isomers seems to be large enough for separation of some phenolic compounds, although HPLC is often able to resolve a number of well-known examples already (e.g. catechin and epicatechin). To confirm, which isomer is in cis- or trans-configuration, a standard would be needed; this measurement was not done within the work for this thesis.

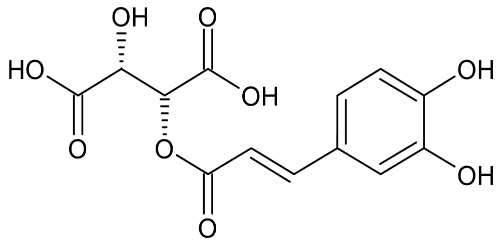


Figure 3.14.: Chemical structure of caftaric acid, sumformula $C_{13}H_{12}O_9$, exact mass of the $[M-H]^-$ ion 311.0409 m/z.

Table 3.7.: These extracted ions are plotted in the **Fig. 3.15** and used for the tentative identification of caftaric acid.

Caftaric acid	spectrum	fragmentation frame	drift range [ms]	mass range [m/z]	retention time range [min]	sample
1	drift	no fragmentation	-	311.0122-311.0792	4.130-4.220	shiraz
2	drift	low	-	310.0747-315.2867	4.121-4.251	shiraz
3	drift	low	-	311.0307-311.0551	4.103-4.233	blaufränkisch-zweigelt-merlot
4	drift	low	-	311.0158-311.0950	4.115-4.245	blaufränkisch-zweigelt
5	drift	high	-	177.9796-181.7891	4.115-4.245	blaufränkisch-zweigelt
6	drift	high	-	178.9224-179.1582	4.103-4.233	blaufränkisch-zweigelt-merlot
7	drift	high	-	147.0991-150.7254	4.121-4.268	shiraz
8	drift	high	-	148.9520-149.0954	4.115-4.245	blaufränkisch-zweigelt
9	drift	high	-	148.9232-149.2312	4.103-4.233	blaufränkisch-zweigelt-merlot
10	drift	high	-	177.4422-181.0738	4.121-4.268	shiraz
11	drift	low	-	307.0519-316.5457	4.103-4.233	blaufränkisch-zweigelt-merlot
12	drift	high	-	178.9871-179.0935	4.103-4.233	blaufränkisch-zweigelt-merlot
13	drift	high	-	148.9401-149.1510	4.103-4.233	blaufränkisch-zweigelt-merlot
1	EIC	no fragmentation	21.06-22.14	311.0248-312.0799	-	shiraz
2	EIC	low	19.25-20.22	311.0230-312.0965	-	shiraz
3	EIC	low	19.49-19.98	311.0291-311.0718	-	blaufränkisch-zweigelt-merlot
4	EIC	low	21.30-21.78	311.0228-311.0594	-	blaufränkisch-zweigelt
5	EIC	low	20.58-21.06	311.0291-311.0779	-	shiraz
6	EIC	low	-	148.9343-149.0914	-	shiraz
7	EIC	low	-	178.9905-179.1038	-	shiraz
8	EIC	high	-	178.9905-179.1038	-	shiraz
9	EIC	high	-	148.9343-149.0914	-	shiraz
10	EIC	high	20.58-21.06	311.0291-311.0779	-	shiraz
11	EIC	high	19.25-20.22	311.0230-312.0965	-	shiraz
1	mass	no fragmentation	18.41-22.86	-	4.130-4.220	shiraz
2	mass	low	17.93-23.83	-	4.121-4.251	shiraz
3	mass	low	19.01-22.38	-	4.103-4.233	blaufränkisch-zweigelt-merlot
4	mass	low	18.65-23.95	-	4.115-4.245	blaufränkisch-zweigelt
5	mass	high	18.65-23.95	-	4.115-4.245	blaufränkisch-zweigelt
6	mass	high	17.93-23.83	-	4.121-4.251	blaufränkisch-zweigelt-merlot
7	mass	high	19.13-22.14	-	4.103-4.233	shiraz

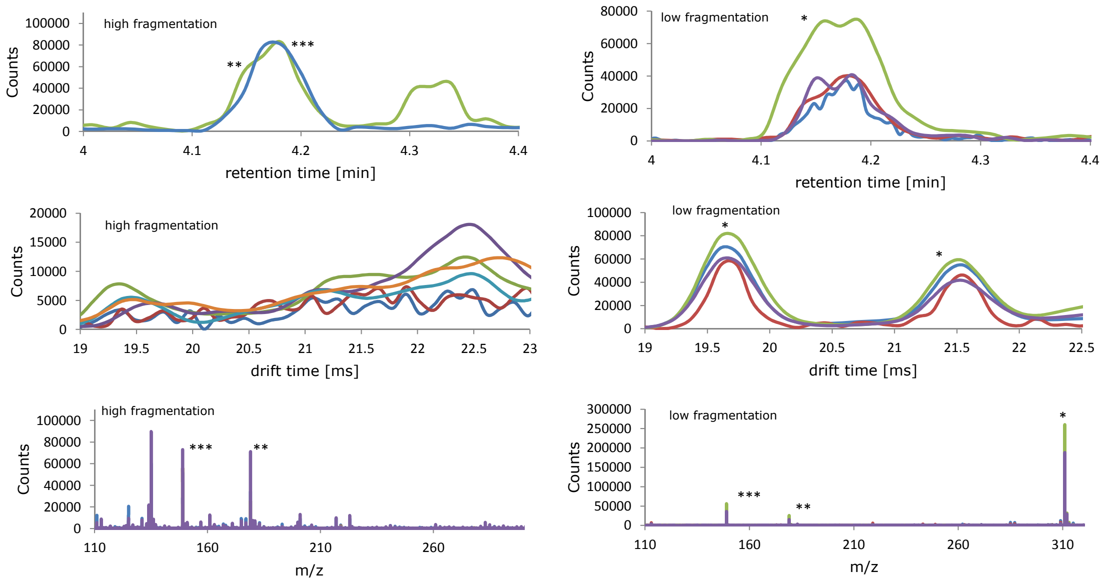


Figure 3.15.: Caftaric acid was chosen to investigate, if the two isomers (cis/trans) would separate in the drift domain. The extracted spectra show, that in this case the chromatography alone is not able to achieve base line separation, whereas the two isomers are clearly separated in the drift domain. The plotted ions with their respective extraction windows can be observed in **Table 3.7**.

3.7.5. Castavinol

Castavinols are substances found in wine and the extracted mass, would match the proposed sumformula well. However, this example is highly speculative as the algorithm of the Mass Hunter Workstation Version B.07.00, could not assign a sumformula with enough confidence. Nevertheless the example was chosen to show, that the chromatography again is not totally reliable, but the drift spectra are clear and are even showing a separation of two compounds. The abundance in this case was very low, so only the wine with the highest abundance showed peaks in IMS mode and locked fragmentation could only be extracted for one fragment each in that same sample.

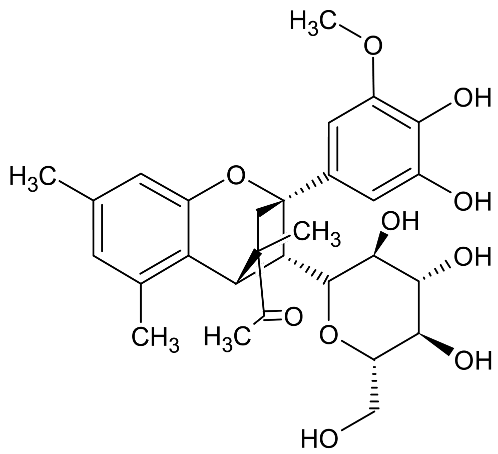


Figure 3.16.: Chemical structure of a castavinol, sumformula $C_{26}H_{30}O_{14}$, exact mass of the $[M-H]^-$ ion 565.1557 m/z.

Table 3.8.: These extracted ions are plotted in the **Fig. 3.17** and used for the tentative identification of castavinol.

Castavinol	Spectrum	fragmentation frame	drift range [ms]	mass range [m/z]	retention time range [min]	sample
1	drift	no fragmentation	-	564.9652-565.3513	6.660-6.883	shiraz
2	drift	low	-	565.1125-565.1947	6.636-6.835	blaufränkisch-zweigelt-merlot
3	drift	high	-	286.9796-287.1552	6.636-6.835	blaufränkisch-zweigelt-merlot
4	drift	high	-	288.5857-290.6674	6.636-6.835	blaufränkisch-zweigelt-merlot
1	EIC	no fragmentation	27.92-28.76	565.1363-565.2102	-	shiraz
2	EIC	high	26.35-27.44	565.1249-566.2180	-	shiraz
3	EIC	low	26.35-27.44	565.1249-566.2180	-	shiraz
4	EIC	low	27.20-27.80	565.1332-565.1825	-	blaufränkisch-zweigelt-merlot
5	EIC	high	27.20-27.80	565.1332-565.1825	-	blaufränkisch-zweigelt-merlot
1	mass	low	21.18-31.65		4.520-4.598	shiraz
2	mass	high	21.18-31.65		4.520-4.598	shiraz

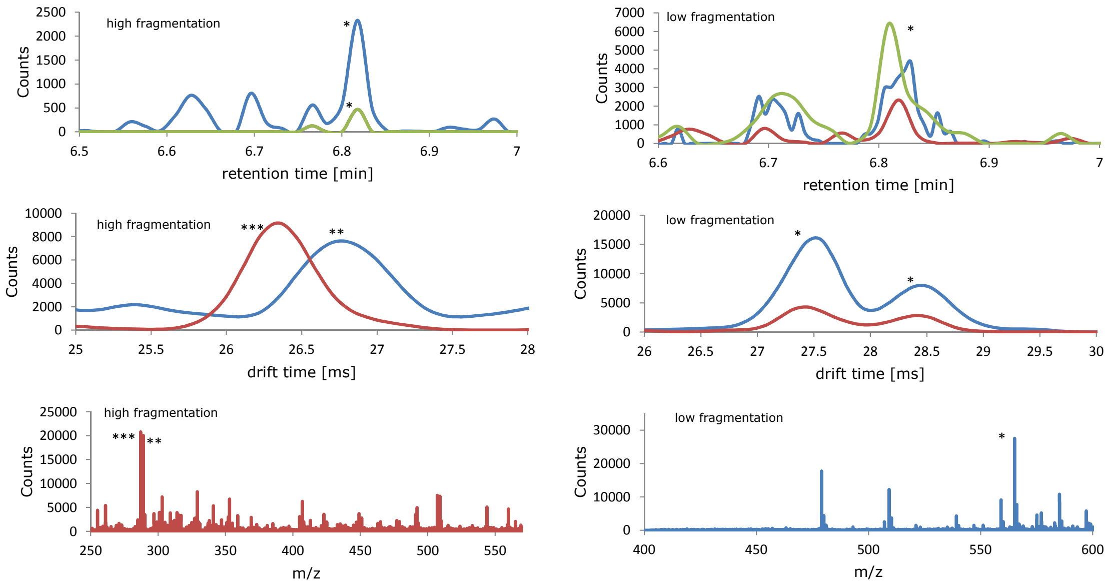


Figure 3.17.: Castavinol is proposed as a candidate for this spectra combination. Due to low abundance the chromatography in this case has no satisfying signal-to-noise ration, therefore the drift spectra can be used to obtain information. The plotted ions with their respective extraction windows can be observed in **Table 3.8**.

4. Conclusion

The major goal of this thesis was, assessing how useful the additional ion mobility separation for further, feature alignment and annotation is. Through the usage of drift time t_d and the corresponding calculation of the CCS values, a new identification parameter can be introduced to a analytical workflow. Moreover, repeatability of t_d within a sample group can be used to improve the quality of untargeted and targeted data sets.

The possibility of adding drift information and alternating frames fragmentation with LC-IM-QTOF to a feature, seems promising not only for identification, also to acquire additional information for substance class grouping and further separation of the samples with the chance to resolve isobaric compounds. Still the method parameters need adjustment to improve transmission and the use of IM multiplexing will be the most powerful option to address this with the current instrumental setup.

Then the additional separation in the drift tube can be a valuable asset to solve analytical problems. Especially cleaning mass spectra by drift time filtering is dramatically improving signal-to-noise ratio as the majority of the background ions are removed. The fact that the separation in the drift tube takes only milliseconds makes it a time saving option in comparison to LCxLC-systems, even though they have higher peak capacities. Finally the option exists to run the instrument itself with an LCxLC-system to improve separation further. There are a lot of possibilities to use ion mobility in targeted and untargeted approaches and the resolving power for phenolic extracts was satisfactory at least, comparing results between labs could also be improved as less reliance is placed on chromatographic reproducibility due to the very high precision of the drift time separation.

Appendix A.

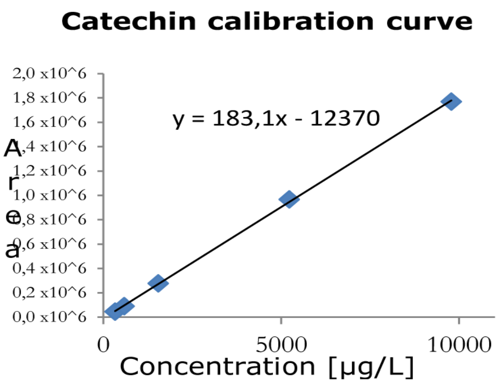
Chemicals

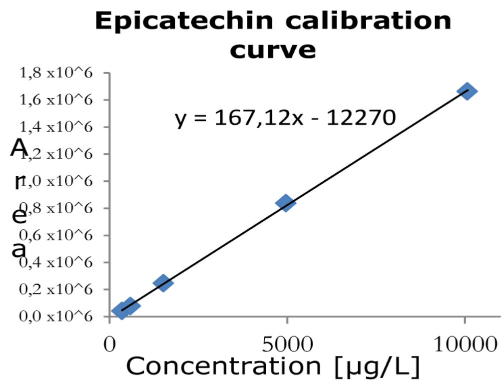
Name	Provider	Code	Molecular mass	Purity	Batch #
p-Coumaric acid	Fluka	28200	164.16	$\geq$ 98 %	1315296
Gallic acid monohydrate	Roth	7300.1	188.13	$\geq$ 98 %	32789741
Quercetin dihydrate	Sigma	Q0125	338.26	$\geq$ 98 %	085K0720
(+)-Catechin Hydrate	Fluka	22130	290.28	$\geq$ 96 %	1282200
(-)-Epicatechin	Sigma	E1753	290.28	$\geq$ 98 %	1354271
Naringenin	SAFC	W530098	272.25	$\geq$ 96 %	KBG5459V
Kaempherol	Sigma	60010	286.24	$\geq$ 96 %	1424445
Myricetin	Sigma	M6760	318.24	$\geq$ 99 %	1420459
Rutin hydrate	SIGMA	R5143	610.52	$\geq$ 99 %	086K1245
Ammonium Formate	Fluka	09735	63.06	$\geq$ 99 %	1365019
Trifluoro-m-toluic acid	SIGMA	188344	190.12	$\geq$ 99 %	454922
Water LC-MS Chromasolv	Fluka	39253		$\geq$ 99 %	7732185
Acetonitril LC-MS Chromasolv	Fluka	34967			75058
Methanol HiPerSolv Chromanorm	VWR	83638.32			14Z4188
Formic acid	Fluka	56302			67561

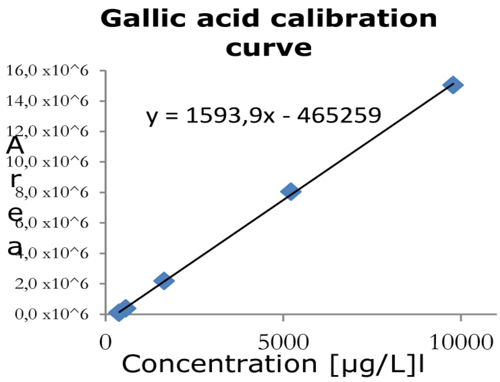
Appendix B. Quantification

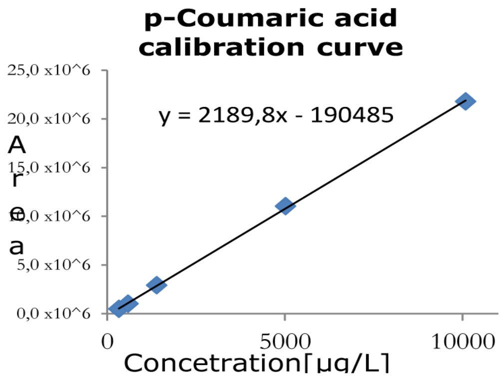
Sample					Gallic acid			Epicatechin Results			Catechin Results		
Name	Data File	Type	Level	Acq. Date-Time	RT	Final Conc.	Area	RT	Final Conc.	Area	RT	Final Conc.	Area
STD5	003_STD5.d	Cal	5	7.20.2015 2:34 PM	1,396	387,266138	104112,02	5,775	353,643933	41156,77	7,036	333,80471	42806,15
STD4	005_STD4a.d	Cal	4	7.20.2015 3:23 PM	1,357	572,7077325	415728,13	5,703	538,351634	75683,94	6,98	549,57466	86315,16
STD4	006_STD4b.d	Cal	4	7.20.2015 3:47 PM	1,377	561,562623	392581,6	5,723	563,719652	79084,99	7	567,94016	88690,46
STD4	007_STD4c.d	Cal	4	7.20.2015 4:12 PM	1,36	568,0664997	370479,68	5,739	599,583946	78290,33	7	584,56161	84352,09
STD4	008_STD4d.d	Cal	4	7.20.2015 4:36 PM	1,351	567,2094653	363588,93	5,747	586,578311	75095,83	7,024	591,10729	84174,24
STD4	009_STD4e.d	Cal	4	7.20.2015 5:01 PM	1,362	570,0073828	364657,24	5,724	580,708957	73577,14	7,018	596,4718	84375,07
STD4	010_STD4f.d	Cal	4	7.20.2015 5:25 PM	1,371	574,4036625	363763,61	5,733	565,370067	69831,09	6,994	576,39317	79421,71
STD4	011_STD4g.d	Cal	4	7.20.2015 5:50 PM	1,37	583,6369582	414953,58	5,733	576,511161	78707,91	7,01	575,27705	87226,1
STD4	012_STD4h.d	Cal	4	7.20.2015 6:14 PM	1,355	582,1606522	405236,81	5,718	606,932355	82225,29	6,979	616,72804	93012,81
STD4	013_STD4i.d	Cal	4	7.20.2015 6:39 PM	1,349	589,5650611	427611,96	5,728	612,817214	85362,19	7,022	598,00969	92048,39
STD4	014_STD4j.d	Cal	4	7.20.2015 7:03 PM	1,368	595,6662191	415099,59	5,748	631,707617	84012,83	7,025	626,47981	92296,68
STD4	015_STD4k.d	Cal	4	7.20.2015 7:28 PM	1,361	585,2198145	411238,06	5,74	621,702594	84881,32	7,017	613,59815	92745,64
STD3	017_STD3.d	Cal	3	7.20.2015 8:17 PM	1,345	1652,677281	2195086,3	5,741	1520,24326	245418,4	7,018	1553,4223	276265,8
STD2	018_STD2.d	Cal	2	7.20.2015 8:41 PM	1,362	5226,661831	8038592,2	5,741	4968,39275	836568,8	7,002	5231,3725	966523,2
STD1	019_STD1.d	Cal	1	7.20.2015 9:06 PM	1,346	9783,188679	15036663	5,725	10073,7366	1662158	7,003	9785,2591	1768102

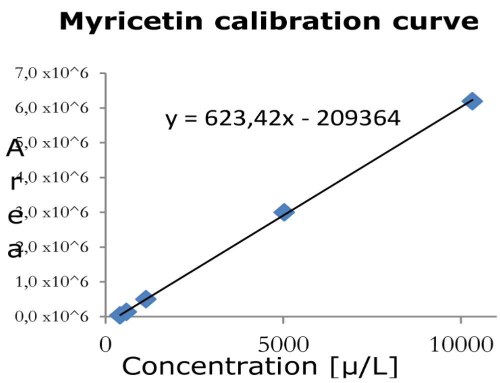
p-Coumaric acid Results			Myricetin Results			Quercetin Results			Naringenin Results			Kaempherol Results		
RT	Final Conc.	Area	RT	Final Conc.	Area	RT	Final Conc.	Area	RT	Final Conc.	Area	RT	Final Conc.	Area
7,65	336,25909	475972,73	10,287	415,932302	33447,17	11,963	337,0806	114878,8	13,14	318,9764	907390,83	13,572	219,93852	644582,31
7,61	552,608875	995667,8	10,264	579,348909	140756,1	11,956	600,64709	301769,6	13,117	565,4749	1739021,1	13,549	639,84842	1486796,7
7,63	551,082212	980169,44	10,251	570,695097	133547,2	11,96	547,79869	262570,1	13,137	557,12808	1692062,7	13,585	577,04859	1350523,3
7,63	614,073065	1029911,9	10,251	602,496809	141299,5	11,96	585,9421	264865,6	13,137	608,98652	1702497,1	13,569	691,26583	1438689
7,638	605,95241	997859,77	10,259	586,419946	129905,5	11,967	587,12557	261559,8	13,145	585,60374	1611110,9	13,576	612,43078	1282515,8
7,632	618,788096	1015304,4	10,269	592,016096	132022,1	11,978	576,70008	253103,3	13,139	589,00112	1607215	13,57	646,30865	1329137,9
7,641	606,12197	970462,72	10,278	580,67046	123080,7	11,97	554,92685	235242,2	13,148	582,45032	1557750,1	13,579	558,64298	1157787,7
7,64	615,091897	1087671,9	10,261	578,314022	134037,1	11,953	570,72442	269243,3	13,147	603,03731	1776500,5	13,562	610,99023	1369937,1
7,626	581,940301	997822,22	10,263	591,470017	139587,5	11,955	635,74283	306002,1	13,133	597,16045	1727358,6	13,581	607,21314	1338622,9
7,652	589,834312	1041210,3	10,257	584,563693	138967,6	11,949	579,63723	277209,6	13,126	589,50118	1749560,3	13,558	563,13437	1292766,7
7,655	600,480535	1010400,8	10,243	613,249656	148810,4	11,968	623,18823	290281,9	13,129	625,80396	1764940,7	13,577	598,5549	1288970,3
7,647	625,555362	1093780,1	10,268	609,302512	150835	11,96	602,40778	285568,1	13,138	553,8211	1604724,3	13,569	529,95973	1204032,2
7,648	1396,12185	2906294,8	10,269	1140,98075	503004	11,978	1553,5888	952183,1	13,156	1725,9968	5385835,4	13,587	1690,5958	3495646,7
7,632	5018,97736	11046047	10,253	5032,05827	2995083	11,961	5614,8837	3702198	13,139	5330,9389	16616159	13,57	5954,0493	11574234
7,616	10087,1127	21778567	10,254	10322,4815	6194751	11,979	9429,6061	6100643	13,14	9566,1193	28944879	13,588	8900,0188	16652344

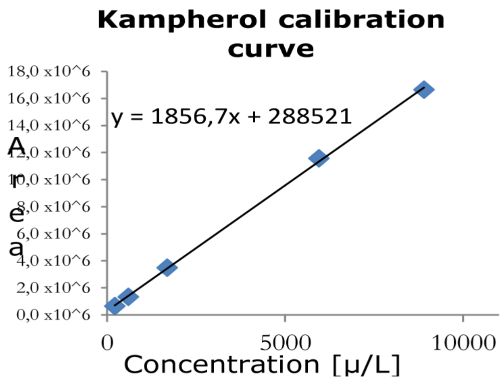

Catechin calibration curve
y = 183,1x - 12370
Area
Concentration [µg/L]

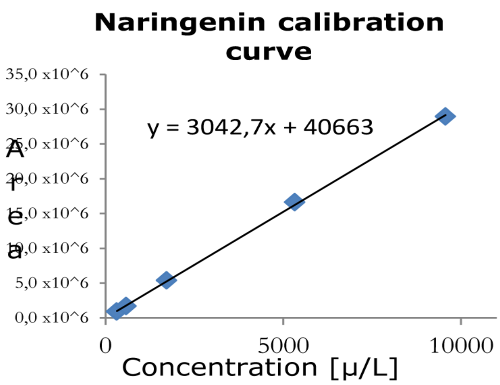

Epicatechin calibration curve
y = 167,12x - 12270
Area
Concentration [µg/L]

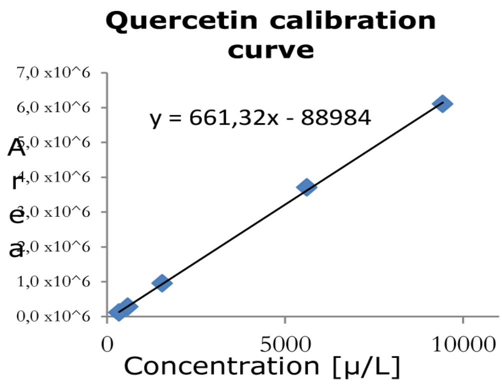

Gallic acid calibration curve
y = 1593,9x - 465259
Area
Concentration [µg/L]l


p-Coumaric acid calibration curve
y = 2189,8x - 190485
Area
Concetration[µg/L]


Myricetin calibration curve
y = 623,42x - 209364
Area
Concentration [µ/L]


Kampherol calibration curve
y = 1856,7x + 288521
Area
Concentration [µ/L]


Naringenin calibration curve
y = 3042,7x + 40663
Area
Concentration [µ/L]


Quercetin calibration curve
y = 661,32x - 88984
Area
Concentration [µ/L]

Appendix C.

CCS single field calibration

Figure C.1.: All measured calibrant ions plotted in a t_d against reciprocal field strength difference $1/\Delta V$ plot.

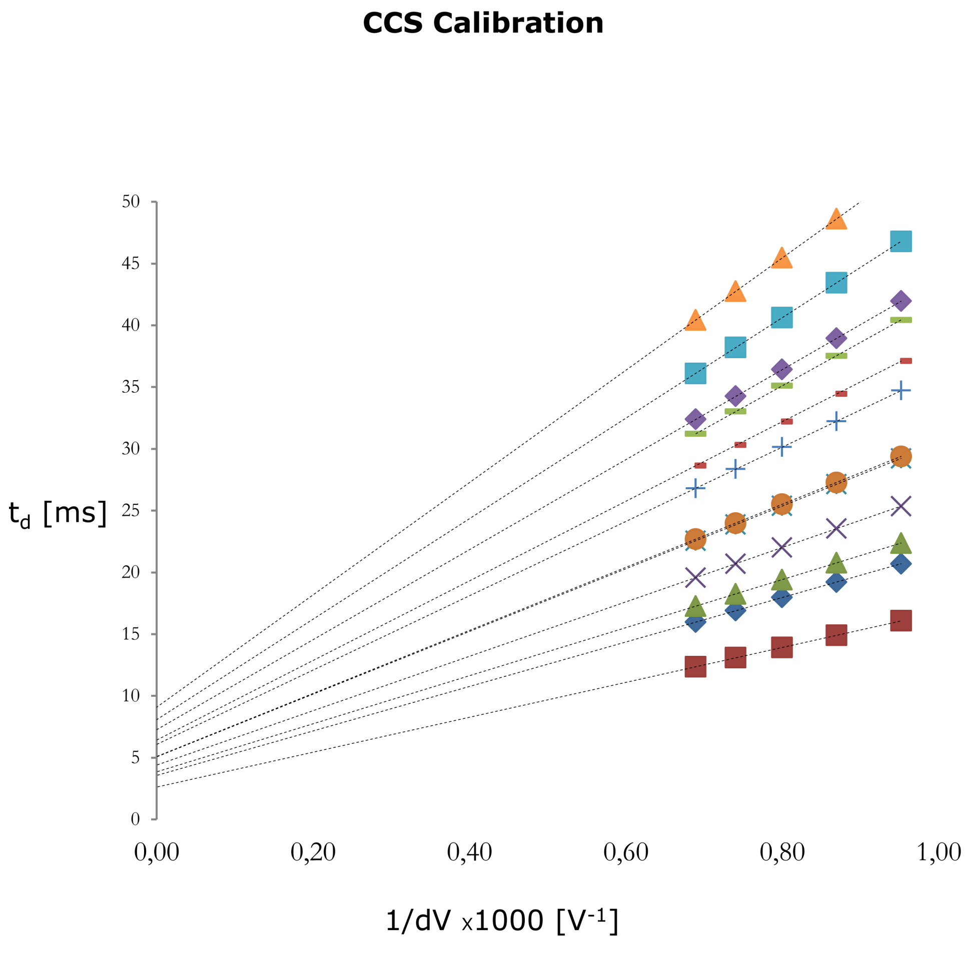


Table C.1.: Calibration used for the LC-IM-QTOF method with and without alternating frames mode on.

# Single-Field CCS Calibration Data							
# Results							
Points Used	6						
Beta	0,127949						
TFix	-0,562799						
TFix SE	0,11038215						
# Scalar Inputs							
Ion Polarity	Negative						
Drift Gas	N2						
Point ID	CCS (A²)	m/z	Ion Species	Mass	z	tD (ms)	Residual (ms)
1	128,7	169,0142	(M-H)-	169,0137	1	14,8	0,111
2	169,4	301,0354	(M-H)-	301,0349	1	20,09	-0,0788
3	172,3	317,0303	(M-H)-	317,0298	1	20,43	-0,1392
4	215,7	709,9426	(M-H)-	709,9421	1	26,61	0,103
5	230,4	805,9907	(M-H)-	805,9902	1	28,43	0,0126
6	250,1	955,972	(M-H)-	955,9715	1	30,97	-0,0085

Table C.2.: Calibration used for the LC-IM-QTOF method for the repeatability measurements, with six wine samples from the same wine.

# Single-Field CCS Calibration Data							
# Results							
Points Used	5						
Beta	0,126337						
TFix	-0,069953						
TFix SE	0,060531508						
# Scalar Inputs							
Ion Polarity	Negative						
Drift Gas	N2						
Point ID	CCS (A²)	m/z	Ion Species	Mass	z	tD (ms)	Residual (ms)
1	128,7	169,0142	(M-H)-	169,0137	1	14,94	-0,0497
2	143	301,9981	(M-H)-	301,9976	1	17,21	-0,0027
3	183,5	601,979	(M-H)-	601,9785	1	22,68	0,0883
4	259,7	1033,988	(M-H)-	1033,9875	1	32,28	-0,0243
5	288,9	1333,969	(M-H)-	1333,9685	1	36,04	-0,0116

Table C.3.: Stepped-field measurements of the calibrant ions used for the single-field calibration.

m/z	Point ID	tD(ms, obs)	E (V/cm)	dV (V)	td (ms)	Ko	CCS (A²)
112,9855	1	12,36	18,595	1450,4	9,74	2,025	111
	2	13,08	17,313	1350,4	10,46	2,025	111
	3	13,92	16,03	1250,3	11,3	2,024	111
	4	14,9	14,748	1150,3	12,28	2,025	111
	5	16,07	13,467	1050,4	13,45	2,025	111
m/z	Point ID	tD(ms, obs)	E (V/cm)	dV (V)	td (ms)	Ko	CCS (A²)
248,9603	1	15,97	18,595	1450,4	12,41	1,589	133,5
	2	16,9	17,313	1350,4	13,34	1,588	133,6
	3	17,97	16,03	1250,3	14,41	1,588	133,6
	4	19,22	14,748	1150,3	15,66	1,588	133,6
	5	20,7	13,467	1050,4	17,14	1,589	133,5
m/z	Point ID	tD(ms, obs)	E (V/cm)	dV (V)	td (ms)	Ko	CCS (A²)
301,9981	1	17,26	18,595	1450,4	13,41	1,471	142,9
	2	18,26	17,313	1350,4	14,41	1,47	143
	3	19,41	16,03	1250,3	15,56	1,471	143
	4	20,76	14,748	1150,3	16,91	1,471	143
	5	22,37	13,467	1050,4	18,52	1,471	143
m/z	Point ID	tD(ms, obs)	E (V/cm)	dV (V)	td (ms)	Ko	CCS (A²)
384,9349	1	19,57	18,595	1450,4	15,17	1,3	160,2
	2	20,7	17,313	1350,4	16,3	1,3	160,3
	3	22	16,03	1250,3	17,6	1,3	160,3
	4	23,53	14,748	1150,3	19,13	1,3	160,3
	5	25,35	13,467	1050,4	20,95	1,3	160,3
m/z	Point ID	tD(ms, obs)	E (V/cm)	dV (V)	td (ms)	Ko	CCS (A²)
520,9108	1	22,56	18,595	1450,4	17,49	1,128	183,1
	2	23,86	17,313	1350,4	18,79	1,128	183,1
	3	25,37	16,03	1250,3	20,3	1,127	183,2
	4	27,13	14,748	1150,3	22,06	1,128	183,1
	5	29,22	13,467	1050,4	24,15	1,128	183,1
m/z	Point ID	tD(ms, obs)	E (V/cm)	dV (V)	td (ms)	Ko	CCS (A²)
601,979	1	22,68	18,595	1450,4	17,58	1,122	183,4
	2	23,98	17,313	1350,4	18,88	1,122	183,4
	3	25,51	16,03	1250,3	20,41	1,121	183,6
	4	27,28	14,748	1150,3	22,18	1,121	183,5
	5	29,37	13,467	1050,4	24,27	1,122	183,4
m/z	Point ID	tD(ms, obs)	E (V/cm)	dV (V)	td (ms)	Ko	CCS (A²)
709,9426	1	26,81	18,595	1450,4	20,74	0,951	215,7
	2	28,35	17,313	1350,4	22,28	0,951	215,7
	3	30,14	16,03	1250,3	24,07	0,95	215,8
	4	32,23	14,748	1150,3	26,16	0,951	215,8
	5	34,71	13,467	1050,4	28,64	0,951	215,7
m/z	Point ID	tD(ms, obs)	E (V/cm)	dV (V)	td (ms)	Ko	CCS (A²)
805,9907	1	28,64	18,595	1450,4	22,2	0,888	230,3
	2	30,3	17,313	1350,4	23,86	0,888	230,5
	3	32,21	16,03	1250,3	25,77	0,888	230,5
	4	34,45	14,748	1150,3	28,01	0,888	230,5
	5	37,1	13,467	1050,4	30,66	0,888	230,4
m/z	Point ID	tD(ms, obs)	E (V/cm)	dV (V)	td (ms)	Ko	CCS (A²)
955,972	1	31,22	18,595	1450,4	24,18	0,816	250,1
	2	33,01	17,313	1350,4	25,97	0,816	250,1
	3	35,1	16,03	1250,3	28,06	0,816	250,2
	4	37,52	14,748	1150,3	30,48	0,816	250,1
	5	40,43	13,467	1050,4	33,39	0,816	250,2
m/z	Point ID	tD(ms, obs)	E (V/cm)	dV (V)	td (ms)	Ko	CCS (A²)
1033,9881	1	32,38	18,595	1450,4	25,12	0,785	259,6
	2	34,25	17,313	1350,4	26,99	0,785	259,7
	3	36,42	16,03	1250,3	29,16	0,785	259,8
	4	38,94	14,748	1150,3	31,68	0,785	259,7
	5	41,95	13,467	1050,4	34,69	0,785	259,6
m/z	Point ID	tD(ms, obs)	E (V/cm)	dV (V)	td (ms)	Ko	CCS (A²)
1333,9689	1	36,1	18,595	1450,4	28,02	0,704	288,7
	2	38,2	17,313	1350,4	30,12	0,703	289
	3	40,61	16,03	1250,3	32,53	0,703	288,9

Appendix D.

Feature lists

D.1. Shiraz

D.1.1. LC-IM-(Q)TOF

Feature	RT	DT	m/z	Abund	Ω [$\AA^2$]	Z	Quality	Mass	Ions
1	11.202	15.76	189.0159	996826	129	1	100	190.0232	3
2	9.694	20.09	301.0353	928088	161.5	1	100	302.0426	3
3	11.2	23.11	401.0197	761695	184.4	1	100	402.027	3
4	8.413	20.43	317.0285	548220	164	1	100	318.0358	4
5	11.115	21	315.0496	455077	168.7	1	75	316.0569	4
6	6.41	16.7	197.044	390376	136.5	1	99.71	198.0513	3
7	4.556	15.48	175.0604	349030	127.3	1	100	176.0677	2
8	5.19	19.16	289.0684	324704	154.1	1	100	290.0757	3
9	10.915	19.77	285.0397	271098	159.3	1	100	286.047	3
10	6.34	22.44	366.1181	267561	179.5	1	100	367.1254	3
11	6.006	19.16	289.0715	233550	154.1	1	100	290.0788	3
12	7.417	25.29	477.0637	231581	201.1	1	100	478.071	4
13	4.555	23.32	373.1087	198709	186.5	1	100	374.116	3
14	4.962	27.54	577.1285	178828	218.3	1	100	578.1357	3
15	6.785	25.31	479.0802	147128	201.3	1	94.8	480.0874	3
16	4.323	28.21	616.1058	129045	223.4	1	100	617.113	3
17	7.566	27.15	497.3315	124195	215.9	1	98.98	498.3388	3
18	5.444	15.81	179.0342	105606	129.8	1	100	180.0415	3
19	11.161	17.75	257.0026	101857	143.3	1	79.29	258.0098	3
20	11.198	14.3	161.0214	101381	117.9	1	94.52	162.0287	2
21	8.212	22.4	389.1222	99411	178.8	1	100	390.1295	2
22	11.199	24.53	469.0084	99252	195.1	1	78.43	470.0157	2
23	5.013	24.18	443.1869	95749	192.5	1	100	444.1942	3
24	5.015	21	295.0419	93033	169.2	1	75	296.0492	2
25	8.129	26.83	507.1127	92929	213.2	1	99.36	508.1199	3
26	5.811	27.74	577.1325	84383	219.9	1	100	578.1397	4
27	4.025	20.99	315.107	81757	168.6	1	100	316.1143	3
28	3.689	19.58	305.0649	79275	157.2	1	100	306.0722	2
29	4.177	20.03	333.0211	75031	160.4	1	92.26	334.0284	2
30	6.1	23.39	384.2474	73483	186.9	1	72.64	385.2546	2
31	11.402	19.34	242.175	73371	157	1	100	243.1823	2
32	7.496	25.97	493.0963	71595	206.5	1	94.03	494.1036	3
33	5.503	22.28	325.0906	71311	179	1	96.67	326.0978	2
34	7.276	19.03	300.9977	64676	152.7	1	97.88	302.0049	3
35	3.378	23.9	429.1585	64231	190.5	1	75.74	430.1658	2

36	9.757	21.26	331.0446	64148	170.5	1	96.28	332.0519	2
37	4.177	19.66	311.0386	61234	157.7	1	78.94	312.0459	2
38	3.323	23.22	399.1485	59859	185.3	1	99.98	400.1558	2
39	4.325	27.93	638.0881	58077	220.9	1	87.72	639.0953	3
40	3.542	22.4	385.1337	57837	178.9	1	95.69	386.141	2
41	4.104	16.98	219.0504	53378	138	1	76.23	220.0577	1
42	5.819	22.26	325.0914	52421	178.8	1	96.25	326.0987	3
43	7.521	28.73	625.1741	52123	227.5	1	100	626.1814	3
44	6.338	24.15	434.1048	51762	192.4	1	96.08	435.112	3
45	3.594	27.69	591.0994	50575	219.4	1	90.49	592.1066	3
46	11.247	19.65	318.9726	50544	157.5	1	67.28	319.9799	2
47	9.687	27.35	603.0763	50446	216.5	1	100	604.0836	3
48	4.174	21.54	311.0383	49990	173.2	1	100	312.0456	2
49	5.188	21.28	357.0542	49777	170.2	1	75	358.0614	3
50	7.092	27.27	497.3294	46200	216.9	1	94.88	498.3366	3
51	3.824	27.69	593.1286	45785	219.4	1	97.02	594.1359	2
52	11.2	29.47	613.026	44993	233.5	1	68.75	614.0333	2
53	7.418	25.73	499.046	44304	204.4	1	100	500.0533	2
54	5.696	24.56	401.1428	43008	196.2	1	93.5	402.15	2
55	4.939	20.04	293.1203	42593		0	70.11	293.1208	1
56	11.198	15.69	145.0265	40961		0	70.52	145.0271	1
57	5.696	24.86	447.1482	39988	198	1	100	448.1555	3
58	6.004	21.28	357.0573	39908	170.2	1	100	358.0646	2
59	9.76	17.77	207.0661	37659	145.1	1	93.57	208.0734	2
60	9.686	22.78	369.0224	37480	182.2	1	94.11	370.0297	2
61	4.05	28.6	633.1116	36508	226.4	1	90.08	634.1189	4
62	3.27	24.94	487.1636	36272	198.2	1	63.87	488.1709	2
63	3.706	18.21	243.0503	35873	147.5	1	57.47	244.0576	2
64	4.424	24.42	373.1109	35824	195.5	1	84.67	374.1181	2
65	7.718	23.83	353.1218	35757	191.1	1	100	354.1291	2
66	7.356	24.96	463.0845	33418	198.6	1	71.99	464.0918	3
67	5.975	24.56	431.1907	32304	195.7	1	71.46	432.1979	2
68	5.282	26.44	509.1252	29904		0	67.3	509.1258	1
69	5.861	26.99	511.1447	28275	214.5	1	54.2	512.152	2
70	6.191	16.21	189.0763	28228	132.7	1	82.22	190.0836	2
71	10.78	22.27	327.2165	27823	178.8	1	80.05	328.2238	3
72	5.426	24.54	427.1804	27680	195.7	1	100	428.1877	2
73	4.551	27.37	571.1582	27612		0	79.74	571.1587	1
74	11.39	22.42	329.2323	27591	180.1	1	76.63	330.2396	2
75	3.444	20.94	315.0706	27510	168.2	1	65.55	316.0779	2
76	4.174	15.82	179.0339	26709	130	1	73.46	180.0412	2
77	5.757	24.92	431.1903	25947		0	79.66	431.1909	1
78	4.602	17.63	265.0284	25769	142.1	1	61.41	266.0357	2
79	6.716	25.27	479.0787	24965	200.9	1	78.5	480.086	2
80	4.174	27.63	623.0851	24915	218.7	1	85.3	624.0923	2
81	3.858	25.15	487.0641	24761		0	69.16	487.0647	1
82	3.725	21.27	357.0781	24240	170.1	1	100	358.0854	2
83	7.537	24.27	449.106	23927	193.2	1	61.79	450.1133	2
84	5.176	24.66	484.0974	23649	195.9	1	79.23	485.1047	2
85	4.977	19.57	305.0622	23386	157.1	1	81.22	306.0695	2
86	5.506	19.99	265.0706	22140	161.6	1	62.7	266.0779	2
87	7.785	22.54	363.0709	21791		0	50.47	363.0715	1
88	4.03	22.3	383.0947	21667		0	75.9	383.0953	1

89	4.664	27.89	593.1247	21460	221	1	86.63	594.132	3
90	11.112	23.51	383.0359	21236	187.9	1	74.65	384.0432	2
91	8.106	16.66	187.0973	21016		0	78.43	187.0978	1
92	6.739	25.7	493.0586	20874	204.3	1	95.87	494.0658	3
93	6.521	15.47	163.0379	20738	127.8	1	86.42	164.0451	2
94	8.209	24	457.109	20515	190.9	1	100	458.1162	2
95	7.418	28.98	625.1731	20503	229.5	1	79.86	626.1804	3
96	4.523	17.63	265.0289	19507		0	72.85	265.0295	1
97	11.198	29.83	607.0093	19183		0	58.49	607.0099	1
98	3.575	20.94	323.1329	18511		0	77.03	323.1335	1
99	5.953	19.81	319.044	18101		0	74.24	319.0445	1
100	4.583	22.07	395.0911	17980	176	1	74.64	396.0984	2
101	5.824	19.97	265.0702	17575	161.4	1	58.2	266.0774	2
102	7.276	15.11	167.0349	17502		0	51.66	167.0355	1
103	6.027	24.11	429.2098	17355	192.1	1	85.37	430.2171	2
104	5.149	20.75	323.1308	17151	166.4	1	84.93	324.1381	2
105	6.338	25.22	502.0914	16776		0	61.37	502.0919	1
106	3.596	21.6	368.0963	16614		0	74.79	368.0969	1
107	5.211	23.87	451.119	16109	189.9	1	80.17	452.1262	2
108	11.361	15.75	189.0164	15897	128.9	1	56.7	190.0237	2
109	5.547	24.03	481.0945	15789	190.9	1	93.29	482.1018	2
110	4.551	26.84	565.1421	14776	212.8	1	78.54	566.1494	2
111	6.096	23.92	487.1429	14653	189.9	1	93.36	488.1501	2
112	3.829	22.26	423.0586	14422		0	73.77	423.0591	1
113	7.436	27.84	595.1627	14385		0	69.2	595.1632	1
114	4.139	27.74	593.1274	14253	219.8	1	65.31	594.1346	2
115	5.249	20.07	325.0895	14240	160.8	1	86.78	326.0968	2
116	4.906	23.52	373.1083	13318	188.2	1	86.24	374.1156	2
117	7.495	26.59	509.221	13280		0	54.35	509.2216	1
118	7.527	28.6	579.1685	13208	226.9	1	83.41	580.1758	2
119	5.051	23.24	367.155	12995	186	1	92.18	368.1623	2
120	4.509	26.53	509.1275	12783	210.8	1	84.11	510.1348	2
121	7.697	19.45	243.0646	12691	157.8	1	92.44	244.0719	2
122	5.46	25.13	447.1491	12651	200.2	1	57.68	448.1564	2
123	6.036	23.99	487.1428	12648	190.5	1	52.08	488.1501	2
124	7.151	23	403.1001	12577	183.5	1	70.76	404.1074	2
125	8.553	24.04	433.1107	12572		0	70.18	433.1113	1
126	3.541	21.68	339.127	12523	173.7	1	50.58	340.1343	2
127	9.697	24.25	430.9917	12346		0	55.6	430.9922	1
128	4.524	19.31	326.9989	11944		0	54.73	326.9995	1
129	4.534	22.11	395.0914	11611	176.3	1	56.02	396.0987	2
130	4.834	22.61	341.0844	11582		0	70.39	341.085	1
131	11.156	21.19	386.9592	11339		0	65.7	386.9598	1
132	11.154	18.33	273.9923	11122	147.6	1	50.53	274.9995	2
133	5.249	21.96	393.0755	11078		0	67.11	393.076	1
134	7.627	25.61	455.2105	11050		0	60.62	455.211	1
135	11.235	25.95	530.9778	10930		0	50.39	530.9784	1
136	4.1	18.49	243.0481	10810		0	72.32	243.0486	1
137	4.412	19.99	305.017	10769	160.6	1	54.15	306.0243	2
138	4.782	18.06	243.0465	10653		0	80.71	243.0471	1
139	7.164	25.78	435.1251	10230	205.6	1	68	436.1324	2
140	5.146	22.57	341.0839	10041		0	79.53	341.0844	1
141	4.784	19.41	305.0158	9796	155.8	1	73.62	306.0231	2

142	6.491	25.41	461.161	9783	202.3	1	61.15	462.1683	2
143	8.072	19.86	287.1484	9753		0	85.59	287.1489	1
144	6.008	21.53	329.0855	9627	172.7	1	100	330.0928	2
145	4.148	26.65	553.0779	9553	211.3	1	59.7	554.0851	3
146	3.659	23.55	430.0415	9501		0	56.21	430.042	1
147	7.165	25.21	441.1939	9452		0	81.31	441.1944	1
148	6.739	16.12	173.0808	9414		0	88.77	173.0813	1
149	4.408	18.63	243.0485	9352		0	60.75	243.0491	1
150	4.278	23.81	413.1629	9317	189.9	1	52.95	414.1701	2
151	4.537	22.52	411.057	9150		0	68.96	411.0576	1
152	8.495	23.84	435.1276	9100		0	81.54	435.1282	1
153	11.264	17.42	191.0708	8998		0	69	191.0713	1
154	7.447	23.98	449.1988	8990	190.8	1	50.19	450.2061	2
155	5.814	25.03	393.0771	8927		0	65.64	393.0776	1
156	4.159	13.9	149.0084	8893		0	81.52	149.0089	1
157	9.702	22.73	301.0346	8828	183.3	1	60	302.0418	2
158	3.442	17.09	230.0125	8817		0	50.14	230.0131	1
159	4.239	15.44	175.0606	8747		0	54.33	175.0611	1
160	6.816	27.43	509.2204	8510		0	80.09	509.221	1
161	6.7	22.6	347.1149	8362		0	69.22	347.1155	1
162	4.83	20.06	295.0432	8209	161.4	1	55.58	296.0505	2
163	4.104	24.94	461.0889	8118	198.5	1	55.52	462.0962	2
164	5.505	24.97	393.0772	8113		0	69.97	393.0778	1
165	5.819	27.06	551.1358	7880	214.7	1	53.45	552.1431	3
166	11.608	15.76	189.0161	7845		0	63.47	189.0167	1
167	7.78	21.21	333.0598	7836	170.1	1	97.4	334.067	2
168	3.572	22.04	391.1203	7769		0	68.36	391.1209	1
169	4.495	17.74	244.0265	7590		0	60.41	244.0271	1
170	14.769	14.08	174.956	7575		0	53.53	174.9565	1
171	15.196	14.09	174.9543	7518		0	68.73	174.9548	1
172	3.95	20.45	323.1332	7288		0	79.5	323.1338	1
173	2.976	17.67	229.0321	7225	143.4	1	51.97	230.0394	2
174	5.188	22.34	425.0411	7175		0	87.62	425.0417	1
175	5.236	20.23	307.0218	7087		0	81.35	307.0223	1
176	6.004	14.49	153.0187	6904		0	66.69	153.0193	1
177	4.09	20.7	370.9894	6751		0	52.82	370.9899	1
178	6.821	27.5	565.1522	6723	218.1	1	65.54	566.1594	2
179	15.534	14.01	174.9559	6568		0	58.56	174.9565	1
180	5	23.15	385.009	6520		0	51.47	385.0095	1
181	3.8	18.48	241.032	6494		0	57.33	241.0325	1
182	11.07	19.5	378.9167	6428		0	52.4	378.9173	1
183	4.201	15.66	183.0292	6374	128.4	1	76.4	184.0365	2
184	8.15	26.87	508.1168	6371		0	66.52	508.1173	1
185	6.509	31.35	737.136	6329	247.8	1	60.36	738.1433	3
186	9.266	21.56	331.114	6259		0	53.45	331.1146	1
187	8.243	29.35	639.1893	6134	232.4	1	74.13	640.1966	2
188	15.071	14.07	174.9546	6134	115.3	1	54.14	175.9618	2
189	3.528	21.83	347.095	6113		0	57.06	347.0955	1
190	12.908	21.62	315.1795	5852		0	70.53	315.18	1
191	6.933	29.04	619.1303	5574	230	1	53	620.1376	2
192	6.574	18.84	261.132	5504		0	67.29	261.1325	1
193	3.093	21.12	390.9973	5433		0	50.31	390.9979	1
194	3.97	21.47	393.0485	5422	171.2	1	58.7	394.0558	2

195	5.263	21.32	329.0836	5397	171	1	54.97	330.0908	2
196	4.168	23.69	382.0964	5324	189.4	1	59.3	383.1037	1
197	8.15	18.44	243.1233	5302		0	53.85	243.1238	1
198	10.338	28.48	537.2706	5264	226.3	1	61.53	538.2779	2
199	6.004	20.62	289.0704	5204	166.2	1	53.57	290.0777	1
200	3.314	24.9	487.165	5182	197.8	1	56.97	488.1723	2
201	11.778	19.49	378.9166	5170		0	73.73	378.9172	1
202	5.172	25.35	506.0761	5160	201.3	1	66.77	507.0834	2
203	6.44	24.45	433.2058	5148	194.8	1	79.58	434.2131	2
204	4.824	20.7	385.0114	5098		0	63.2	385.0119	1
205	11.686	17.79	231.0085	5011		0	53.76	231.0091	1
206	5.433	14.24	135.0452	4964		0	54.15	135.0458	1
207	14.616	14.07	174.9536	4927	115.3	1	53.88	175.9608	2
208	15.513	13.97	174.9544	4887		0	65.16	174.9549	1
209	6.307	16.17	165.055	4882		0	62.93	165.0555	1
210	13.708	14.35	180.9725	4868		0	57.27	180.9731	1
211	3.154	21.16	390.9968	4854		0	51.5	390.9974	1
212	3.173	15.8	156.067	4839		0	53.97	156.0676	1
213	4.934	21.86	361.1074	4757		0	66.94	361.108	1
214	12.926	14.31	180.9724	4752		0	82.29	180.973	1
215	2.619	19	287.0335	4732	152.8	1	55.21	288.0408	2
216	4.576	26.87	565.1413	4708	213	1	56.95	566.1486	2
217	3.175	18.84	291.0039	4670		0	57.73	291.0044	1
218	11.755	14.35	180.9729	4648		0	85.67	180.9734	1
219	6.339	31.2	733.2424	4545	246.6	1	51.83	734.2497	1
220	2.31	18.62	312.9835	4473		0	53.24	312.984	1
221	15.801	13.98	174.9556	4447		0	50.16	174.9562	1
222	9.826	14.32	180.9732	4424		0	51.88	180.9738	1
223	3.196	17.62	229.0326	4416		0	53.3	229.0332	1
224	14.411	15.25	218.932	4386		0	57.53	218.9325	1
225	6.154	24.81	453.1165	4386	197.5	1	68.24	454.1238	2
226	13.203	25	449.155	4332		0	56.46	449.1555	1
227	5.631	29.3	644.1353	4218		0	71.83	644.1359	1
228	6.937	22.46	397.0597	4217		0	72.16	397.0603	1
229	5.288	18.83	257.0616	4047		0	68.22	257.0622	1
230	10.367	14.29	180.9736	4018		0	57.78	180.9741	1
231	3.669	20.75	331.0651	4016		0	53.62	331.0657	1
232	6.05	23.92	381.1734	3964		0	83.34	381.1739	1
233	14.461	14.32	180.973	3962		0	52.18	180.9735	1
234	7.056	17.94	204.0654	3902		0	73.12	204.066	1
235	15.489	15.15	216.9344	3827		0	50.73	216.935	1
236	6.125	22.28	398.0222	3811		0	74.27	398.0227	1
237	11.146	22.7	454.9475	3809		0	52.53	454.948	1
238	4.524	19.54	333.0156	3798	156.3	1	80.17	334.0229	2
239	6.415	20.2	280.9959	3749		0	62.22	280.9964	1
240	3.05	14.42	153.0193	3734		0	50.87	153.0199	1
241	11.17	23.63	416.9945	3726		0	53.98	416.995	1
242	14.189	14.32	180.9725	3715		0	85.26	180.9731	1
243	6.603	22.85	574.1011	3704		0	55.81	574.1016	1
244	8.084	18.63	277.0658	3660		0	71.46	277.0663	1
245	6.174	25.11	399.1267	3639		0	59.75	399.1272	1
246	4.928	20.05	294.1244	3636	161.3	1	53.8	295.1317	2
247	13.888	14.35	180.9741	3606		0	61.43	180.9746	1

248	4.292	21.56	373.1093	3601		0	70.26	373.1098	1
249	13.979	15.15	216.9337	3551		0	52.51	216.9343	1
250	3.712	21.78	373.0522	3536		0	68.9	373.0527	1
251	7.085	27.5	514.3195	3500	218.6	1	50.26	515.3268	2
252	2.698	18.98	287.0328	3470	152.7	1	51.38	288.0401	2
253	15.285	19	242.0813	3441		0	55.18	242.0818	1
254	8.28	17.54	211.0589	3423		0	51.08	211.0594	1
255	11.459	22.62	329.2323	3396	181.7	1	87.01	330.2396	2
256	6.757	28.62	559.1051	3392		0	51.65	559.1056	1
257	4.111	19.63	305.0174	3374		0	78.43	305.0179	1
258	3.648	22.69	383.154	3359		0	50.32	383.1545	1
259	11.534	15.77	189.0166	3319		0	56.42	189.0172	1
260	2.878	21.91	412.9779	3310		0	53.63	412.9784	1
261	5.23	15.79	193.0127	3291	129	1	63.99	194.02	2
262	3.908	21.34	377.0056	3287		0	52.35	377.0062	1
263	13.239	15.13	216.9337	3284		0	53.23	216.9342	1
264	6.099	23.51	401.2362	3273		0	59.17	401.2368	1
265	3.746	19.57	305.0653	3254	157.1	1	52.99	306.0726	2
266	14.881	14.33	180.9736	3249		0	51.84	180.9742	1
267	8.161	18.65	265.1046	3244		0	53.58	265.1051	1
268	11.465	17.77	257.0036	3235		0	79.02	257.0041	1
269	6.381	23.72	423.1854	3223		0	78.33	423.1859	1
270	5.721	22.31	397.0573	3109		0	53.01	397.0579	1
271	8.262	14.26	180.9738	3104		0	70.15	180.9743	1
272	2.359	17.05	251.0146	3101		0	53.34	251.0151	1
273	14.527	14.23	180.9724	3084		0	64.66	180.9729	1
274	11.793	14.25	180.9753	3080		0	85.42	180.9758	1
275	13.432	14.32	180.9735	3074		0	60.79	180.9741	1
276	6.817	28.44	565.1516	3071	225.7	1	65.93	566.1589	1
277	15.596	14.19	174.956	3063		0	53.35	174.9566	1
278	2.415	19.57	309.0132	3033		0	50.98	309.0137	1
279	11.097	17.74	310.9283	3008		0	59.6	310.9288	1
280	11.231	18.72	298.9921	2981		0	57.6	298.9927	1
281	13.982	19.5	378.9179	2981		0	59.2	378.9184	1
282	15.082	13.12	154.9743	2945		0	53.29	154.9749	1
283	15.778	14.32	180.9728	2944		0	69.33	180.9734	1
284	12.793	14.32	180.9735	2916	117.1	1	55.38	181.9808	1
285	15.589	19.57	378.9156	2883		0	52.1	378.9161	1
286	3.449	15.25	153.055	2883		0	50.24	153.0555	1
287	4.969	26.42	577.1305	2877	209.2	1	60.94	578.1377	1
288	12.521	15.14	216.9344	2868		0	50.77	216.9349	1
289	13.973	14.34	180.9724	2867		0	50.54	180.9729	1
290	3.223	20.08	358.9891	2865		0	64.06	358.9897	1
291	3.175	17.12	219.0517	2833		0	72.84	219.0522	1
292	15.87	15.16	216.9332	2786		0	55.24	216.9337	1
293	11.167	23.15	403.0263	2764		0	58.13	403.0269	1
294	4.646	20.84	315.0704	2761		0	59.65	315.071	1
295	15.996	22.75	353.1985	2741	182.2	1	59.26	354.2058	2
296	6.678	14.34	180.9731	2740		0	90.12	180.9737	1
297	6.124	17.65	304.9102	2719		0	51.38	304.9107	1
298	4.211	16.91	181.0504	2701		0	50.13	181.051	1
299	12.95	19.52	378.9174	2646		0	79.44	378.918	1
300	15.748	14.33	180.9729	2645		0	85.91	180.9734	1

301	13.422	14.43	191.9454	2645		0	50.42	191.946	1
302	6.019	19.18	291.0761	2632		0	60.43	291.0766	1
303	11.308	14.3	180.973	2632		0	79.68	180.9736	1
304	3.853	22.89	341.0823	2610		0	66.71	341.0828	1
305	6.818	14.32	180.9722	2598		0	72.68	180.9727	1
306	11.584	15.79	189.0162	2595		0	75.73	189.0168	1
307	12.803	31.43	982.9863	2593	247.3	1	55	983.9936	2
308	6.735	17.78	257.0305	2590	143.5	1	64.37	258.0378	2
309	2.092	23.87	369.1381	2585		0	67.28	369.1386	1
310	4.95	21.88	361.1078	2580		0	68.76	361.1084	1
311	4.907	18.84	275.0062	2573		0	57.73	275.0067	1
312	13.487	14.32	180.9736	2547		0	71.41	180.9741	1
313	11.33	14.35	180.9723	2505		0	82.18	180.9728	1
314	15.459	15.21	216.934	2476		0	55.99	216.9345	1
315	11.178	24.82	607.0064	2474		0	51.71	607.0069	1
316	12.382	14.35	180.9728	2469		0	63.52	180.9733	1
317	15.913	14.34	180.9724	2458		0	62.59	180.9729	1
318	12.361	17.72	310.9285	2415		0	77	310.9291	1
319	14.452	19.56	378.918	2399		0	82.68	378.9185	1
320	13.155	19.5	378.9168	2375		0	56.79	378.9173	1
321	6.245	14.31	180.9728	2343		0	54.62	180.9733	1
322	4.116	16.94	220.0535	2313		0	54.5	220.054	1
323	11.147	19.77	257.0007	2286		0	82.1	257.0013	1
324	3.403	18.95	296.0157	2259		0	65.15	296.0163	1
325	3.924	18.47	241.0313	2250		0	54.72	241.0319	1
326	11.549	17.72	257.0024	2245		0	56.25	257.003	1
327	4.238	21.53	311.0377	2228		0	54.95	311.0382	1
328	5.191	19.16	289.1796	2224		0	56.92	289.1801	1
329	4.977	25.23	479.075	2224		0	55.97	479.0755	1
330	6.946	20.8	315.0694	2217		0	87.88	315.07	1
331	11.246	16.98	189.0172	2215	139.2	1	57.95	190.0245	1
332	13.466	14.32	180.9727	2214		0	85.75	180.9733	1
333	7.673	14.23	180.9729	2202		0	50.23	180.9735	1
334	4.23	19.35	326.9973	2181		0	57.96	326.9978	1
335	15.65	13.13	119.0355	2161		0	50.04	119.036	1
336	11.246	17.75	189.0156	2145	145.8	1	51.09	190.0229	1
337	4.991	23.57	446.9786	2143		0	70.2	446.9791	1
338	11.35	18.35	273.9924	2128		0	57.7	273.9929	1
339	6.949	14.33	180.9731	2120		0	58.34	180.9737	1
340	10.064	20.14	301.035	2114		0	50.95	301.0356	1
341	4.319	22.75	616.1054	2113	179.4	1	53.14	617.1127	1
342	4.124	17.29	211.0597	2095		0	57.64	211.0603	1
343	9.144	14.34	180.9732	2091		0	57.17	180.9737	1
344	8.371	14.42	180.9725	2057		0	57.46	180.973	1
345	13.385	14.33	180.9724	2036		0	62.22	180.9729	1
346	3.227	18.89	291.0015	2033		0	67.4	291.002	1
347	2.167	23.14	481.0548	2020		0	75.73	481.0553	1
348	5.989	17.7	304.9114	1997		0	72.17	304.9119	1
349	3.176	22.4	345.0808	1972		0	54.88	345.0813	1
350	10.372	19.57	378.9143	1949		0	66.6	378.9148	1
351	11.654	20.85	446.9038	1933		0	52.49	446.9044	1
352	11.735	15.76	189.0176	1926		0	61.38	189.0181	1
353	5.008	23.82	452.9971	1924	189.4	1	57.8	454.0044	2

354	15.837	14.06	174.9562	1922		0	51.19	174.9567	1
355	13.559	19.08	394.8896	1916		0	53.68	394.8902	1
356	4.526	17.77	259.0124	1906		0	57.55	259.013	1
357	8.832	20.45	317.0273	1901		0	70.5	317.0278	1
358	4.467	22.33	440.991	1891		0	59.46	440.9916	1
359	2.835	19.52	378.9152	1887		0	64.66	378.9157	1
360	3.869	18.3	296.9889	1878		0	89	296.9894	1
361	5.546	14.38	180.9722	1869		0	91.96	180.9728	1
362	15.374	14.32	180.9727	1852		0	67.51	180.9733	1
363	3.009	17.62	247.0118	1847		0	63.65	247.0124	1
364	6.212	25.25	495.0173	1845		0	68.02	495.0178	1
365	4.883	19.76	472.0681	1844		0	56.13	472.0686	1
366	7.035	14.33	180.9724	1841		0	52.96	180.973	1
367	13.49	18.67	236.1055	1835		0	50.77	236.106	1
368	11.938	15.78	189.0155	1820		0	72.2	189.016	1
369	3.852	18.53	241.0326	1816		0	78.92	241.0332	1
370	4.159	19.6	312.0425	1808		0	54.05	312.043	1
371	5.872	19.45	241.1174	1801		0	52.22	241.118	1
372	13.967	15.78	230.9552	1783		0	93.82	230.9558	1
373	12.524	15.72	230.9556	1753		0	57.71	230.9562	1
374	4.928	17.48	213.0358	1749		0	54.53	213.0363	1
375	2.669	19.58	378.9152	1742		0	66.83	378.9158	1
376	5.958	17.6	304.9126	1741		0	52.4	304.9131	1
377	6.699	21.9	369.0949	1737		0	57.81	369.0955	1
378	6.325	20.97	362.9991	1732		0	59.38	362.9996	1
379	3.326	29.73	658.0918	1715	235.3	1	69.06	659.099	2
380	4.599	17.73	259.0114	1713		0	78.15	259.0119	1
381	10.356	17.78	310.9292	1696	142.3	1	54.79	311.9365	2
382	9.624	18.07	248.9607	1688		0	51.5	248.9612	1
383	2.883	18.17	258.9914	1680		0	90.65	258.9919	1
384	15.61	15.21	218.9303	1671		0	55.58	218.9308	1
385	14.281	13.37	135.9701	1669		0	50.28	135.9707	1
386	7.787	23.43	453.0391	1668		0	55.85	453.0397	1
387	4.546	17.68	244.0277	1663		0	52.81	244.0282	1
388	8.321	18.49	231.1583	1653		0	52.44	231.1588	1
389	10.598	16.12	174.9555	1644		0	52.84	174.9561	1
390	8.96	17.76	310.9281	1643		0	57.98	310.9287	1
391	6.336	19.43	295.0114	1628		0	55.9	295.012	1
392	6.422	21.41	348.9806	1627		0	70.47	348.9812	1
393	3.478	20.32	381.9504	1624		0	62.74	381.951	1
394	9.986	14.31	180.9729	1622		0	55.14	180.9734	1
395	6.51	14.23	180.9696	1613		0	52.13	180.9701	1
396	12.231	17.81	310.9279	1609		0	57.07	310.9285	1
397	13.104	15.87	230.9543	1608		0	58.37	230.9549	1
398	11.242	25.79	401.0229	1598		0	51.26	401.0235	1
399	11.909	15.83	189.017	1595		0	74.64	189.0176	1
400	3.427	18.92	296.013	1590		0	67.95	296.0136	1
401	11.678	17.75	310.9285	1582		0	58.68	310.9291	1
402	11.322	18.36	273.9941	1574		0	65.24	273.9946	1
403	5.887	25.12	485.1766	1573		0	52.36	485.1771	1
404	8.341	18.53	231.1592	1557		0	81.62	231.1598	1
405	15.018	15.15	218.9312	1539		0	55.83	218.9318	1
406	2.447	19.04	287.0327	1537		0	77.98	287.0333	1

407	5.793	17.62	304.9137	1533		0	57.93	304.9143	1
408	7.079	17.89	204.065	1533		0	51.63	204.0655	1
409	4.486	23.31	359.096	1531		0	57.55	359.0966	1
410	5.966	15.84	193.013	1526		0	68.77	193.0136	1
411	4.041	22.31	384.0988	1525		0	51.29	384.0993	1
412	5.37	21.88	349.0924	1524		0	63.48	349.093	1
413	3.485	21.67	383.0567	1519		0	56.74	383.0572	1
414	9.916	17.79	310.9288	1513	142.4	1	56.86	311.9361	1
415	13.011	14.24	180.9722	1510		0	69.94	180.9728	1
416	5.597	14.32	180.973	1504		0	71.12	180.9736	1
417	5.941	23.91	419.025	1503		0	56.53	419.0255	1
418	13.861	14.31	180.9733	1489		0	51.18	180.9738	1
419	4.594	23.36	485.061	1471		0	56.75	485.0615	1
420	3.828	16.6	173.0461	1460		0	62.45	173.0467	1
421	14.591	19.49	378.9168	1459		0	67.44	378.9174	1
422	3.207	21.63	380.9726	1449		0	51.06	380.9732	1
423	8.006	24.73	461.07	1399		0	61.37	461.0705	1
424	6.811	26.71	508.1139	1395		0	52.53	508.1145	1
425	10.655	20.24	301.0344	1391		0	54.06	301.035	1
426	11.561	21	315.0499	1390		0	64.78	315.0504	1
427	6.792	16.47	195.062	1389		0	74.28	195.0625	1
428	4.589	23.6	479.0431	1337		0	54.42	479.0437	1
429	4.737	21.3	359.1317	1307		0	59.58	359.1322	1
430	12.566	20.89	446.9035	1306		0	57.3	446.9041	1
431	12.861	15.22	216.9332	1304		0	51.85	216.9338	1
432	6.482	25.09	441.1924	1296	199.9	1	71.29	442.1996	2
433	11.293	19.48	378.9157	1287		0	54.48	378.9163	1
434	6.201	22.26	398.0229	1277		0	63.66	398.0235	1
435	6.085	19.55	478.0714	1273		0	70.42	478.072	1
436	14.206	20.49	440.8862	1262		0	52.72	440.8867	1
437	14.348	15.76	230.9556	1258		0	53.21	230.9561	1
438	4.094	18.81	219.0496	1226	153.3	1	51.75	220.0569	1
439	11.153	27.1	604.9812	1226		0	60.61	604.9817	1
440	14.283	15.88	230.9544	1220		0	58.14	230.9549	1
441	11.635	19.34	242.1756	1213		0	53.03	242.1762	1
442	11.181	17.46	248.9711	1208		0	79.92	248.9716	1
443	11.149	19.35	302.9963	1205		0	62.11	302.9969	1
444	5.229	18.33	261.0256	1190		0	65.52	261.0261	1
445	3.12	28.89	645.1872	1172		0	61.66	645.1877	1
446	5.577	23.01	406.1615	1168		0	54.43	406.1621	1
447	12.182	15.72	189.0169	1125		0	57.3	189.0174	1
448	7.962	18.53	241.1062	1107		0	71.66	241.1067	1
449	4.221	13.88	149.0082	1100		0	71.25	149.0088	1
450	4.549	27.82	581.116	1100		0	56.77	581.1165	1
451	14.981	16.96	194.0828	1096		0	63.17	194.0834	1
452	4.661	20.92	345.1153	1090		0	68	345.1159	1
453	5.565	19.18	241.1163	1066		0	64.63	241.1168	1
454	6.619	16.74	197.0438	1065		0	50.68	197.0443	1
455	5.893	19.41	241.1178	1044		0	50.2	241.1183	1
456	4.101	21.02	379.0206	1042	167.7	1	73.55	380.0279	2
457	3.717	18.64	241.0332	1032		0	55.62	241.0338	1
458	6.397	18.04	261.015	1016		0	68.13	261.0155	1
459	8.55	24.31	394.146	1016		0	53.44	394.1466	1

460	2.334	16.73	188.0939	992	0	56.77	188.0945	1
461	10.144	19.85	271.0604	985	0	51.37	271.061	1
462	2.459	18.97	269.0236	964	0	56.2	269.0241	1
463	11.301	14.27	161.0208	953	0	63.32	161.0214	1
464	9.788	19.72	269.1378	953	0	67.06	269.1383	1
465	3.802	20.62	300.0797	948	0	50.38	300.0803	1
466	3.464	18.94	296.0141	911	0	61.49	296.0147	1
467	5.068	20.02	294.1239	909	0	50.83	294.1244	1
468	11.352	17.82	258.0036	891	0	52.3	258.0041	1
469	6.196	23.19	389.1759	884	0	50.84	389.1765	1
470	5.748	22.35	359.0958	881	0	52.04	359.0964	1
471	5.373	18.68	409.0553	878	0	55.79	409.0559	1
472	3.89	16.58	229.0019	877	0	51.01	229.0024	1
473	3.504	17.17	231.0148	868	0	55.43	231.0153	1
474	3.888	16.73	235.0191	864	0	51.2	235.0196	1
475	6.072	19.16	290.0733	858	0	62.9	290.0738	1
476	5.164	23.65	584.1187	853	0	50.98	584.1192	1
477	11.152	24.54	401.0206	842	0	50.14	401.0211	1
478	3.118	19.85	350.9637	834	0	50.56	350.9642	1
479	11.273	17.04	189.0162	821	0	63.56	189.0167	1
480	12.896	21.7	316.1825	818	0	58.33	316.1831	1
481	4.184	17.21	330.0127	806	0	50.27	330.0132	1
482	12.529	15.76	189.0174	806	0	52.26	189.018	1
483	15.349	18.02	316.8945	805	0	54.4	316.8951	1
484	4.293	19.99	488.0648	802	0	51.54	488.0654	1
485	9.064	13.48	164.9259	800	0	56.88	164.9265	1
486	11.386	14.29	161.0206	775	0	50.48	161.0212	1
487	4.888	19.05	273.043	775	0	53.66	273.0435	1
488	7.205	24.35	433.2058	751	0	50.6	433.2064	1
489	8.236	27.78	589.095	699	0	56.37	589.0955	1
490	4.259	15.79	179.0329	692	0	58.8	179.0334	1
491	10.68	20.87	447.9063	654	0	54.92	447.9069	1
492	9.878	15.4	213.0131	645	0	50.25	213.0136	1
493	13.141	22.87	531.882	641	0	53.54	531.8825	1
494	15.635	11.89	178.8409	636	0	56.03	178.8415	1
495	2.113	21.88	339.1269	630	0	53.53	339.1275	1
496	5.499	22.86	326.0921	567	0	52.1	326.0926	1
497	9.778	22.74	301.0347	552	0	50.35	301.0353	1
498	14.23	24.06	325.1827	289	0	69.29	325.1833	1
499	13.946	24.07	325.183	220	0	83.94	325.1835	1
500	5.22	11.19	136.8624	182	0	59.98	136.8629	1

D.1.2. LC-TOF

ID	RT	Mass	Abund	Score
1	11.187	190.0245	31462550	100
2	4.541	176.0687	9609928	100
3	9.679	302.0427	7911017	100
4	11.186	402.03	6298694	100
5	6.395	198.053	4843184	100
6	11.105	316.0582	3096999	100
7	8.398	318.0375	3012739	100
8	4.148	312.0481	2885332	100
9	5.173	290.079	2258237	100
10	6.327	367.1266	2153888	100
11	4.414	130.0266	1761921	100
12	7.407	478.0748	1735933	100
13	4.991	296.0532	1625799	100
14	5.427	180.0427	1611520	100
15	4.945	578.1424	1603301	100
16	4.543	374.1186	1535164	100
17	5.993	290.0791	1524397	100
18	5.492	326.1	1313795	100
19	4.3	617.1161	1261913	100
20	3.377	983.9984	1250877	100
21	5.808	326.1005	1114516	100
22	10.902	286.0482	1049368	100
23	4.091	220.059	1013829	100
24	8.123	508.122	1001569	100
25	4.414	176.069	997588	100
26	6.775	480.0907	991941	100
27	3.388	967.0081	901087	99
28	7.516	626.1852	821835	100
29	5.799	578.1427	764387	100
30	11.186	614.0362	757487	100
31	11.188	470.0175	727848	100
32	9.679	370.0301	672667	100
33	5.005	444.1997	658067	100
34	4.011	316.1161	603939	100
35	6.499	164.0474	595220	100
36	6.175	190.0844	593136	100
37	7.489	494.1061	583346	100
38	5.69	448.1582	580862	100
39	6.306	166.0635	552962	100
40	3.323	430.1685	537577	100
41	6.216	428.0412	535236	100
42	4.415	244.0562	534332	100
43	11.186	608.0192	532936	100
44	3.146	157.0742	499324	100
45	2.266	162.0531	492831	100
46	4.413	374.1189	488070	100
47	11.393	243.1836	459459	100
48	8.202	390.1313	456835	100
49	7.709	354.1317	449339	100
50	2.935	230.0406	427828	100
51	3.384	956.9798	419902	80.7
52	2.936	144.0425	409454	100
53	4.301	639.0984	406779	100
54	11.187	464.0004	399716	100
55	5.173	358.0664	396376	100
56	2.937	162.0531	393585	100
57	6.328	435.1138	383385	100
58	7.412	626.1849	376901	100
59	9.749	208.0737	368623	100
60	4.154	380.0355	366748	100
61	5.97	432.1993	364096	100
62	3.697	220.0588	359423	100
63	7.151	436.1368	354986	100
64	4.804	296.0534	352109	100
65	9.679	416.0354	350412	100
66	5.753	432.1996	339334	100
67	3.418	154.0633	334270	100
68	3.656	306.0739	333046	99.8
69	5.855	512.1529	327358	100
70	5.993	358.0664	326989	100
71	5.316	132.079	322221	100
72	4.037	634.1206	320016	100
73	4.544	1097.0706	316450	100
74	7.407	500.0566	315836	100
75	3.794	594.1372	315161	100
76	3.27	400.1579	313033	100
77	14.847	195.0899	312576	98.6
78	9.748	332.0532	307264	100
79	3.562	592.1097	306951	100
80	4.233	176.0688	302462	100
81	11.187	275.0019	302300	100
82	3.457	231.0206	302098	100
83	11.387	330.2404	295660	100
84	7.247	168.041	294204	100
85	4.543	572.1691	287599	100
86	3.039	154.0267	283453	100
87	8.398	386.0247	274183	100
88	6.138	398.0305	271003	87
89	4.118	112.0162	270685	100
90	11.187	676.0065	270090	100
91	5.995	154.0268	260307	100
92	5.493	394.0872	259960	100
93	13.454	294.1831	254768	100

94	7.491	510.2311	252260	100
95	11.186	820.0249	251320	100
96	5.419	428.1891	248913	100
97	7.346	464.0953	248067	100
98	5.273	510.1374	247558	100
99	4.989	364.0403	244970	100
100	4.927	294.1316	244453	100
101	6.816	510.2312	243320	100
102	11.239	325.999	241888	100
103	7.429	596.1741	241330	100
104	4.1	288.0458	236790	100
105	5.043	414.1737	234147	100
106	7.262	302.0043	228454	80
107	5.809	394.0872	226731	100
108	10.778	328.2248	226238	100
109	3.164	230.0406	224278	100
110	3.192	488.1739	222862	100
111	5.239	326.1003	213656	100
112	11.186	146.0345	212090	100
113	11.102	384.0457	210805	100
114	7.339	204.0998	206800	100
115	7.525	450.1158	206344	100
116	9.679	438.0172	203532	100
117	8.092	188.1051	202046	100
118	5.325	158.0581	197351	100
119	7.768	364.0792	194767	100
120	4.147	150.0169	194081	100
121	4.983	384.0149	193819	90.4
122	3.321	498.1558	190819	100
123	4.153	334.0301	189826	100
124	5.741	296.1473	187017	100
125	9.795	228.079	186086	100
126	3.378	1034.9955	186056	99.4
127	4.645	594.1369	185142	100
128	5.938	320.0529	184094	98.9
129	4.149	646.0782	183860	100
130	3.678	244.0586	183239	99.2
131	4.771	244.0561	182282	100
132	8.134	244.1313	181151	100
133	5.263	414.0256	179439	100
134	6.703	480.0903	177461	100
135	4.194	182.0582	173956	100
136	4.945	646.1297	172670	100
137	6.485	462.1728	171584	100
138	4.303	661.08	170755	96.5
139	6.022	430.2199	169866	100
140	5.161	485.1104	168616	100
141	3.129	220.0585	167038	100
142	11.187	682.0232	167003	100
143	11.194	531.9876	166005	93.7
144	5.69	516.1452	165814	100
145	6.815	510.1372	165601	100
146	11.252	192.0792	163986	100
147	5.62	488.1528	163555	100
148	8.124	576.1092	163327	100
149	4.932	214.0457	162707	100
150	5.006	512.1865	162546	100
151	4.542	566.152	161900	100
152	3.514	280.1158	161605	100
153	6.395	266.0403	161323	100
154	5.516	326.0639	160685	100
155	3.385	207.0537	158939	100
156	4.803	414.1736	158896	100
157	4.011	384.1031	158686	100
158	6.776	548.0775	157718	100
159	6.726	494.0695	156127	100
160	6.499	738.1461	155080	100
161	6.088	488.1527	152052	100
162	5.799	646.1298	150590	100
163	4.821	342.0951	149886	100
164	4.088	176.0687	148446	100
165	8.037	668.1951	148215	100
166	11.228	319.9821	147948	80
167	11.19	538.0047	146914	98.4
168	7.711	340.0795	146863	100
169	6.303	234.0506	145459	100
170	7.625	456.2203	145096	100
171	6.023	488.153	143892	100
172	4.226	652.2573	141720	100
173	4.418	312.044	140460	96.6
174	11.186	418.004	140450	100
175	3.139	482.106	140423	80
176	4.119	594.1371	140216	100
177	4.084	244.056	138945	100
178	5.626	645.1476	138940	100
179	9.262	264.1362	138873	100
180	3.413	316.0797	137996	100
181	7.684	244.0738	137914	100
182	8.545	434.1209	137792	100
183	3.829	488.0735	136683	100
184	5.449	448.1579	136445	100
185	11.144	325.999	136059	100
186	4.127	554.0878	134598	100
187	6.789	508.1214	133880	100
188	4.175	184.0376	133091	100
189	4.419	306.0263	132917	100

190	5.303	316.1158	132853	100	238	3.302	659.1025	102307	95.1
191	7.517	648.1664	132790	100	239	8.082	782.2056	101526	100
192	3.729	866.2061	132352	100	240	5.2	452.1316	100194	100
193	4.156	402.0174	129850	100	241	6.175	258.0713	100017	100
194	6.024	564.2415	129848	100	242	6.011	324.1321	99280	100
195	8.203	458.1184	129192	100	243	8.203	436.1333	98874	100
196	5.939	194.0207	127094	100	244	6.463	540.1476	98512	100
197	4.103	462.0983	126179	100	245	4.413	442.1061	98296	100
198	4.15	180.0427	125723	100	246	2.937	292.0106	98197	100
199	9.68	432.0008	125637	100	247	5.428	248.0299	97420	100
200	7.488	562.0934	125464	100	248	4.118	174.0165	96210	100
201	6.329	503.1009	125448	100	249	6.014	436.2306	96059	100
202	2.938	346.0874	125326	100	250	2.125	174.0165	95938	95.5
203	4.894	374.1212	124818	100	251	3.701	358.0866	95908	100
204	8.109	182.0581	124438	100	252	6.466	494.1415	95792	100
205	7.163	442.2047	124229	100	253	6.786	586.2258	95221	100
206	3.772	400.1579	124207	100	254	4.301	496.1219	94913	100
207	11.19	247.9829	123019	100	255	4.414	1097.0703	94601	100
208	7.338	272.0872	122577	100	256	4.264	326.158	94563	93.1
209	7.424	472.1942	122019	100	257	6.809	566.1632	94355	100
210	6.086	450.1161	121525	100	258	11.185	479.9726	94304	100
211	5.172	404.0715	120725	100	259	11.146	319.982	94237	100
212	4.935	146.0581	119782	100	260	6.752	560.1163	93357	100
213	10.902	354.0349	119631	100	261	5.144	324.1421	93301	94.6
214	6.698	348.1241	119434	100	262	11.245	387.9696	92956	100
215	8.55	441.1634	118436	100	263	5.502	866.2049	91758	100
216	5.137	342.0949	115906	100	264	8.119	478.1107	91566	100
217	4.492	510.1373	113207	100	265	7.151	504.124	91321	100
218	4.963	306.0739	112324	100	266	6.042	428.1893	91172	100
219	7.309	304.0585	112177	100	267	5.172	426.0535	90228	100
220	4.618	880.1728	111885	85.7	268	4.421	374.0139	89905	98
221	6.395	312.0457	111766	100	269	4.523	396.1005	89671	82.9
222	7.045	205.0741	111108	100	270	4.931	314.0978	89400	98.2
223	11.393	311.1703	110846	100	271	6.457	866.2055	89110	100
224	4.584	266.0378	110784	100	272	7.77	658.19	87756	100
225	5.208	132.0789	110391	100	273	2.959	298.0275	87606	87
226	5.315	200.0664	109741	100	274	8.847	228.0792	86803	100
227	7.924	354.1314	109093	100	275	4.096	310.028	85480	84.6
228	9.378	726.2165	108641	100	276	5.809	552.1475	85456	100
229	7.406	782.2057	108105	100	277	8.3	640.2002	85300	80
230	5.994	336.0844	107752	100	278	6.749	248.0899	84854	100
231	7.407	568.0438	107364	100	279	5.991	404.0719	84589	100
232	3.549	324.1422	105788	100	280	4.268	414.1737	83695	100
233	7.516	694.1719	105773	100	281	7.078	782.2048	83577	97
234	7.266	620.136	105730	100	282	4.125	532.1059	83481	100
235	2.948	118.0631	105403	100	283	5.995	330.0949	83385	100
236	5.854	580.1407	103531	100	284	9.177	726.2161	83230	100
237	5.529	482.1061	102446	100	285	5.992	426.0537	82782	100

286	6.57	578.1417	82435	100
287	10.571	272.0684	82178	100
288	5.206	286.0511	82067	100
289	7.617	220.095	82023	100
290	11.188	691.9788	81657	100
291	4.93	276.016	81588	100
292	3.697	288.0455	81402	96.5
293	5.172	336.0843	81188	100
294	2.937	359.9976	80950	100
295	5.172	326.0552	79966	100
296	8.066	288.1574	79885	100
297	3.563	660.0971	79788	100
298	11.188	888.012	79704	97.5
299	8.293	288.0634	79511	100
300	3.193	207.0535	79452	92

D.2. Blaufränkisch-Zweigelt-Merlot

D.2.1. LC-IM-(Q)TOF

Feature	RT	DT	m/z	Abund	Ω [$\AA^2$]	Z	Quality	Mass	Ions
1	11.196	15.77	189.0165	1030453	129	1	100	190.0238	2
2	11.194	23.11	401.0195	771867	184.4	1	99.62	402.0267	3
3	5.188	19.16	289.0705	576781	154.1	1	100	290.0778	3
4	9.688	20.09	301.0343	509223	161.5	1	100	302.0416	3
5	4.169	27.67	623.0857	407698	219	1	100	624.093	3
6	6.002	19.16	289.0706	387339	154.1	1	100	290.0779	3
7	6.408	16.7	197.0432	345966	136.5	1	100	198.0505	3
8	4.956	27.55	577.1313	329952	218.4	1	100	578.1385	3
9	4.551	15.49	175.0606	290715	127.3	1	75	176.0679	3
10	8.411	20.43	317.0291	255515	164	1	100	318.0364	3
11	4.168	19.67	311.0388	209886	157.9	1	71.27	312.0461	1
12	5.808	27.7	577.1324	183068	219.6	1	100	578.1397	2
13	5.443	15.82	179.0333	172913	129.9	1	100	180.0405	3
14	8.212	22.41	389.1223	167531	178.8	1	100	390.1296	3
15	5.003	20.99	295.0431	163742		0	79.99	295.0436	1
16	6.337	22.44	366.1163	149700	179.5	1	100	367.1236	2
17	11.239	17.75	257.0031	146086	143.3	1	51.06	258.0104	2
18	7.563	27.16	497.3323	144242	216	1	100	498.3395	3
19	4.553	23.33	373.1089	141166	186.7	1	100	374.1162	3
20	4.172	29.44	645.0669	134578	233	1	72.7	646.0741	2
21	3.686	19.57	305.0648	129080	157.2	1	97	306.0721	2
22	6.222	23.62	427.0302	116783	188.1	1	80.42	428.0375	2
23	7.414	25.31	477.0646	111931	201.2	1	100	478.0719	2
24	6.09	23.4	384.2478	110633	187	1	69.63	385.2551	2
25	11.193	24.55	469.0088	105481	195.2	1	83.05	470.0161	2
26	9.752	17.76	207.0652	104607	145	1	82.98	208.0725	2
27	3.818	27.71	593.1279	102269	219.6	1	100	594.1352	3
28	3.587	21.62	368.0966	99360	172.7	1	73.54	369.1039	2
29	5.187	21.29	357.0562	97668	170.3	1	100	358.0635	3
30	11.114	21	315.0504	92579	168.6	1	94.17	316.0577	2
31	4.168	15.83	179.034	91439	130.1	1	63	180.0413	2
32	3.37	23.95	429.159	85357	190.9	1	59.92	430.1663	3
33	3.31	23.21	399.1479	84824	185.2	1	93.83	400.1552	3
34	11.395	19.33	242.1754	82299	156.9	1	100	243.1827	2
35	3.858	25.15	487.0645	81664	199.9	1	100	488.0717	3
36	9.803	19.09	227.0707	81044		0	78.48	227.0712	1
37	7.272	19.01	300.9976	80083		0	79.99	300.9981	1
38	3.367	23.54	383.1533	79883	188.2	1	73.69	384.1606	2
39	6.004	21.29	357.0569	76695	170.2	1	100	358.0641	2
40	11.679	17.75	231.0088	73540	144	1	92.56	232.0161	3
41	7.094	27.25	497.3308	72962	216.7	1	81.64	498.3381	2
42	4.196	21.54	311.0387	66929	173.2	1	60.75	312.046	2
43	8.13	26.84	507.1121	61534	213.3	1	79.99	508.1193	1
44	3.525	19.46	279.1075	60273	156.8	1	76.04	280.1147	2
45	4.136	20.03	333.0205	59368	160.4	1	62.68	334.0278	2
46	7.52	28.77	625.1749	58635	227.8	1	100	626.1822	3
47	4.02	20.98	315.1066	51385	168.5	1	56.92	316.1139	3

48	9.753	21.24	331.045	51302	170.3	1	96.63	332.0523	3
49	5.694	24.88	447.1471	49681	198.1	1	95.89	448.1544	3
50	11.198	26.19	401.0217	49295	209.5	1	76.29	402.029	2
51	5.005	24.17	443.1888	48961	192.4	1	100	444.1961	2
52	4.422	24.43	373.11	45321	195.6	1	100	374.1173	2
53	3.721	21.33	357.0772	43710	170.6	1	75.77	358.0844	3
54	4.933	20.06	293.1208	41762		0	79.99	293.1214	1
55	3.594	27.68	591.1006	41642	219.3	1	52.57	592.1079	2
56	8.213	24	457.1078	39671		0	79.99	457.1084	1
57	10.913	19.77	285.0388	38486		0	50.65	285.0393	1
58	5.693	24.56	401.142	37986		0	76.59	401.1425	1
59	3.539	22.4	385.1338	36056	178.8	1	100	386.1411	2
60	4.661	27.87	593.1262	34038	220.8	1	100	594.1335	3
61	11.149	19.62	318.9731	33871	157.3	1	100	319.9804	2
62	11.206	24.84	462.9912	32842	197.6	1	55.85	463.9985	2
63	7.717	21.73	339.0711	32733	174.1	1	76.96	340.0784	1
64	6.337	24.11	434.1034	32537	192	1	88.05	435.1107	3
65	5.529	22.27	325.0537	31651	178.9	1	84.68	326.061	2
66	11.191	15.68	145.0261	30692		0	60.06	145.0267	1
67	8.553	23.99	433.1122	30400	191.1	1	86.29	434.1195	2
68	5.186	27.36	579.1464	30119	216.8	1	54.28	580.1536	3
69	3.858	25.84	509.0476	29097		0	71.41	509.0481	1
70	4.035	22.26	383.0934	27183	177.8	1	59.14	384.1006	2
71	6.817	26.79	509.1268	26209	212.9	1	69.05	510.1341	2
72	5.283	26.43	509.1253	26047	210	1	88.2	510.1325	3
73	7.414	25.76	499.0461	24693	204.6	1	96.08	500.0534	3
74	6.793	26.72	507.1111	23322	212.4	1	92.63	508.1184	2
75	8.096	17.01	209.0788	22676	138.6	1	95.03	210.086	2
76	7.567	27.54	514.3217	22545		0	71.54	514.3222	1
77	7.416	28.97	625.1736	22172	229.4	1	90.45	626.1809	3
78	4.975	19.57	305.0627	21730	157.1	1	92.93	306.07	2
79	11.193	29.84	607.0107	21716	236.6	1	73.16	608.018	2
80	6.514	15.46	163.0382	21311	127.7	1	52.2	164.0455	2
81	6.013	14.46	153.0192	21296		0	74.54	153.0198	1
82	7.158	25.76	435.1258	21244	205.5	1	68.6	436.1331	2
83	4.313	27.94	638.0876	20973	221	1	71.41	639.0948	2
84	11.65	24.1	435.1394	20967	192	1	69.71	436.1467	2
85	4.582	17.67	265.0289	19731	142.4	1	66.4	266.0361	2
86	11.39	21.23	310.1629	19621	170.7	1	64.68	311.1702	2
87	3.451	20.96	315.0703	19617	168.3	1	58.05	316.0775	2
88	8.117	16.35	181.05	19335		0	63.37	181.0506	1
89	7.773	22.51	363.0711	18732	180.1	1	63.96	364.0784	2
90	5.183	20.6	289.0703	18039	166	1	99.15	290.0776	2
91	7.72	20.43	339.0713	17712	163.5	1	67.06	340.0786	2
92	9.686	22.77	369.0209	17054	182.1	1	89.75	370.0282	2
93	3.708	18.22	243.0501	16950		0	65.31	243.0507	1
94	5.002	22.38	363.0296	16871		0	63.41	363.0302	1
95	8.091	23.47	451.1003	16827	186.6	1	69.64	452.1076	2
96	5.009	23.1	385.0109	16644	184.5	1	57.65	386.0182	2
97	5.754	24.89	431.1896	16644		0	79.99	431.1901	1
98	6.579	27.73	577.132	16192	219.8	1	53.53	578.1393	2
99	7.164	25.68	389.1205	16171	205.6	1	62.19	390.1278	2
100	8.108	16.68	187.0979	15174		0	59.74	187.0984	1

101	5.509	22.25	325.0896	14812	178.7	1	55.38	326.0969	2
102	4.439	29.89	701.0993	14806	236.3	1	50.97	702.1065	2
103	11.148	21.19	386.9612	14476	169	1	98.74	387.9685	2
104	5.969	24.61	431.1905	14464		0	53.92	431.191	1
105	4.821	20.04	295.0437	14110	161.2	1	51.62	296.051	2
106	5.447	14.25	135.045	14071		0	66.14	135.0455	1
107	8.073	19.83	287.1483	13972		0	52.8	287.1488	1
108	7.707	23.81	353.1233	13718	190.9	1	77.28	354.1306	1
109	6.946	22.47	397.0587	13377		0	52.87	397.0592	1
110	5.458	25.19	447.1465	13295	200.7	1	85.9	448.1538	2
111	6.736	25.69	493.0591	13024	204.2	1	81.01	494.0664	2
112	6.001	22.4	419.0275	12559		0	83.06	419.028	1
113	6.137	22.71	576.1232	12455	352.3	2	84.34	1154.261	3
114	5.062	20.11	293.1221	12303	161.9	1	85.71	294.1294	2
115	8.863	19.18	227.0707	12131	156.1	1	73.91	228.078	2
116	4.554	26.85	565.1417	12027	212.8	1	100	566.149	2
117	4.444	18.66	243.0468	11926	151.2	1	63.59	244.0541	2
118	5.187	22.31	425.0441	11923		0	77.8	425.0447	1
119	5.301	22.15	397.0556	11580	176.6	1	73.94	398.0629	2
120	7.513	28.63	579.1686	11517		0	66.61	579.1692	1
121	4.088	16.94	219.0498	11481		0	65.24	219.0503	1
122	5.425	24.54	427.1786	11388		0	54.81	427.1792	1
123	4.09	18.5	243.0471	11311		0	85.53	243.0477	1
124	5.009	21.03	296.0463	11295		0	58.28	296.0468	1
125	8.211	23.6	389.1203	11219	188.6	1	64.96	390.1275	1
126	7.563	26.76	487.3034	11218	212.9	1	54.87	488.3107	3
127	11.26	22.73	454.9474	11022		0	53.5	454.948	1
128	4.587	19.3	326.9987	10995	154.5	1	64.68	328.006	2
129	5.996	20.58	289.0706	10905	165.8	1	72.45	290.0779	1
130	4.128	26.63	553.0766	10760		0	73.19	553.0772	1
131	7.489	25.94	493.0961	10631	206.2	1	58.26	494.1033	3
132	11.16	25.95	530.9793	10359	205.9	1	69.17	531.9865	2
133	3.447	15.27	153.0554	10200		0	70	153.0559	1
134	5.395	23.84	451.1191	10084		0	79.99	451.1196	1
135	4.397	18.67	243.0471	9937	151.3	1	51.21	244.0544	1
136	10.581	19.92	271.0602	9928		0	73.1	271.0607	1
137	5.18	22.4	419.027	9692	178.4	1	60.11	420.0342	2
138	4.592	19.52	333.0157	9688		0	59.83	333.0163	1
139	4.454	21.01	323.1334	9625	168.6	1	98.29	324.1407	2
140	11.28	21.19	386.9608	9510	169	1	53.52	387.9681	2
141	10.229	18.73	228.1607	9387		0	53.87	228.1612	1
142	6.098	23.84	487.1425	8991	189.3	1	51.9	488.1498	2
143	7.43	27.84	595.1638	8862	220.6	1	54.78	596.1711	2
144	11.257	21.55	392.9763	8789		0	56.17	392.9769	1
145	11.268	17.49	191.0704	8587	143.5	1	71.74	192.0776	2
146	8.511	20.44	317.0282	8133	164	1	57.21	318.0355	2
147	4.93	21.81	361.1077	8119		0	79.99	361.1082	1
148	9.683	22.81	391.0028	8014		0	84.69	391.0033	1
149	6.583	18.83	261.1326	7855		0	69.41	261.1332	1
150	5.853	14.07	174.9554	7833		0	58.28	174.9559	1
151	5.526	22.83	393.0403	7800		0	62.69	393.0409	1
152	4.214	25.32	515.0767	7785		0	52.53	515.0773	1
153	7.331	20.07	303.0493	7764		0	57.08	303.0499	1

154	4.509	26.51	509.1264	7708	210.6	1	86.31	510.1336	2
155	8.973	18.68	229.0857	7551		0	66.94	229.0862	1
156	6.004	19.8	289.0697	7252	159.4	1	56.27	290.077	2
157	15.825	14.34	180.9729	7211		0	57.71	180.9735	1
158	8.098	18.49	271.0483	7159		0	62.65	271.0489	1
159	6.332	25.2	502.0877	7155		0	54.75	502.0883	1
160	4.354	23.21	707.2211	7119	359.9	2	57.23	1416.4568	3
161	6.747	16.13	173.0811	7065		0	53.2	173.0816	1
162	9.492	21.53	363.0811	7003	172.1	1	50.52	364.0884	2
163	6.361	25.14	441.1925	6940		0	52.75	441.1931	1
164	11.715	18.54	231.103	6913		0	53.93	231.1036	1
165	5.93	24.77	431.1895	6694	197.5	1	50.78	432.1968	2
166	7.625	25.59	455.21	6686		0	83.07	455.2106	1
167	8.137	26.91	508.1146	6634	213.9	1	66.68	509.1218	2
168	6.16	23.41	384.2468	6612	187.1	1	60.91	385.2541	2
169	2.977	22.67	345.0793	6588	181.8	1	64.88	346.0866	2
170	15.821	20.06	265.1471	6427	162.2	1	72.85	266.1543	3
171	5.086	27.35	577.1329	6161	216.8	1	50.52	578.1402	2
172	4.777	19.44	305.017	5959		0	72.2	305.0175	1
173	6.722	16.46	195.0633	5835	134.6	1	75.24	196.0706	2
174	4.067	22.21	383.0938	5797	177.4	1	57.9	384.1011	2
175	10.061	17.74	304.9125	5782		0	53.56	304.913	1
176	11.396	19.8	297.0746	5724		0	69.63	297.0752	1
177	11.146	22.65	454.9476	5721	179.9	1	74.51	455.9549	2
178	7.686	19.42	243.0653	5699		0	55.3	243.0658	1
179	5.631	14.06	174.9545	5654		0	53.14	174.9551	1
180	8.616	27.01	453.1324	5622		0	54.97	453.133	1
181	4.085	19.86	466.0235	5589		0	72.49	466.024	1
182	7.151	23.03	403.1004	5578	183.7	1	50.87	404.1076	2
183	5.148	20.72	323.1329	5569		0	88.13	323.1335	1
184	3.858	16.7	235.0195	5451		0	62.96	235.0201	1
185	11.156	18.68	298.9915	5307		0	58.07	298.992	1
186	9.436	17.64	304.9123	5191		0	53.41	304.9129	1
187	10.693	17.62	304.912	5185		0	51.36	304.9125	1
188	9.419	17.51	223.0944	5168		0	66.87	223.0949	1
189	4.524	24.76	469.0516	5160	196.9	1	56.44	470.0588	2
190	7.258	19.02	302.0004	5153	152.7	1	53.45	303.0077	2
191	6.021	23.99	487.1433	5150	190.4	1	66.98	488.1506	2
192	5.356	25.18	417.1342	5030		0	74.05	417.1348	1
193	4.393	21.83	329.0857	4969		0	51.72	329.0862	1
194	2.631	19.03	287.0336	4927		0	58	287.0342	1
195	11.094	21.03	316.0524	4911		0	55	316.0529	1
196	11.233	15.67	145.0262	4867		0	56.48	145.0268	1
197	14.278	14.32	180.9724	4843		0	59.14	180.9729	1
198	6.564	20.93	319.08	4732		0	67.32	319.0806	1
199	13.925	14.35	180.973	4719		0	58.56	180.9735	1
200	15.841	20.15	265.1474	4677		0	54.46	265.148	1
201	8.138	18.5	243.1223	4622	149.9	1	86.18	244.1296	1
202	15.869	14.32	180.9728	4616		0	59.8	180.9733	1
203	10.996	14.34	180.9732	4565		0	77.49	180.9737	1
204	10.682	14.34	180.9732	4560		0	51.14	180.9738	1
205	8.202	24.04	458.1105	4540	191.2	1	58.44	459.1178	2
206	7.062	17.9	204.0655	4503	146.3	1	51.13	205.0728	2

207	6.191	23.33	384.2464	4500		0	50.27	384.247	1
208	2.494	17.64	304.9123	4472		0	67.08	304.9129	1
209	8.328	18.48	231.1596	4451		0	55.96	231.1601	1
210	8.249	14.32	180.9727	4420		0	66.74	180.9733	1
211	13.472	21.89	293.1746	4338		0	71.3	293.1751	1
212	3.797	14.47	150.0194	4309		0	67.14	150.02	1
213	8.426	14.39	180.973	4298		0	74.15	180.9735	1
214	5.637	24.49	463.1791	4294		0	52.11	463.1797	1
215	6.472	25.27	493.129	4278	200.8	1	70.81	494.1362	1
216	12.246	24.08	435.1405	4255		0	55.71	435.141	1
217	4.506	17.73	244.0258	4248		0	66.42	244.0264	1
218	7.931	14.31	180.9726	4209		0	57.4	180.9731	1
219	8.559	17.63	304.9103	4156		0	75.45	304.9108	1
220	6.01	21.72	323.1226	4134	174.4	1	90.09	324.1299	2
221	8.429	17.63	304.9124	4101		0	51.87	304.913	1
222	5.888	19.38	241.1181	4058	157.3	1	57.84	242.1254	2
223	12.137	19.56	378.9168	3926		0	79.11	378.9174	1
224	10.795	20.46	287.1478	3917		0	52.21	287.1483	1
225	15.974	20.12	265.1465	3880	162.6	1	81.76	266.1538	2
226	4.405	24.3	441.0968	3834	193.5	1	63.92	442.104	2
227	10.668	18.19	237.1093	3805		0	51.57	237.1099	1
228	7.873	26.92	535.1783	3781		0	57.01	535.1788	1
229	11.241	26.42	536.9986	3776		0	75.9	536.9991	1
230	5.496	17.66	304.9114	3757		0	52.68	304.9119	1
231	3.886	19.63	303.0017	3738		0	57.67	303.0023	1
232	11.584	15.75	189.0165	3708	128.8	1	73.43	190.0237	2
233	3.968	17.61	304.9133	3690		0	50.97	304.9138	1
234	13.771	15.16	216.9339	3687		0	50.64	216.9344	1
235	6.484	25.34	461.1608	3685		0	61.43	461.1613	1
236	8.072	20.16	309.1307	3680		0	52.68	309.1312	1
237	6.414	18.11	197.0433	3674	148.4	1	58.75	198.0506	1
238	15.015	14.37	180.9724	3666		0	52.89	180.9729	1
239	4.073	22.29	330.2023	3653		0	50.33	330.2028	1
240	5.663	23.41	576.1207	3608	363.4	2	57.91	1154.256	2
241	5.808	26.29	577.1329	3606	208.2	1	66.26	578.1402	1
242	4.227	16.94	181.0501	3595		0	54.89	181.0507	1
243	4.032	15.34	153.0546	3590		0	52.67	153.0552	1
244	14.234	14.34	180.9735	3571		0	71.76	180.9741	1
245	5.265	22.72	413.0129	3503	181	1	60	414.0201	2
246	15.492	19.51	378.9155	3451		0	79.84	378.916	1
247	4.523	22.49	411.057	3443		0	62.95	411.0576	1
248	5.551	17.67	304.9105	3422		0	52.07	304.9111	1
249	3.19	17.59	229.0318	3365		0	69.6	229.0323	1
250	3.538	17.04	230.0118	3348		0	76.35	230.0123	1
251	4.409	23.86	413.1634	3333		0	63.34	413.1639	1
252	9.078	19.53	378.9146	3316		0	57.93	378.9151	1
253	15.214	15.16	218.9304	3288		0	77.07	218.931	1
254	5.31	19.08	289.0677	3260		0	50.87	289.0683	1
255	11.267	17.8	258.0069	3257	143.6	1	52.79	259.0142	2
256	10.786	17.64	304.9109	3226		0	52.07	304.9115	1
257	2.987	20.56	358.9899	3205	164.2	1	52.88	359.9972	2
258	5.952	21.86	387.0323	3181		0	55.68	387.0328	1
259	15.171	19.59	378.9194	3171		0	59.31	378.9199	1

260	11.698	17.81	235.0031	3160		0	66.57	235.0037	1
261	10.141	19.9	271.0595	3135		0	54.08	271.06	1
262	11.251	15.66	145.0262	3122		0	62.92	145.0268	1
263	14.818	14.38	180.9723	3122		0	58.12	180.9729	1
264	6.449	16.69	198.048	3080		0	52.73	198.0485	1
265	4.92	19.36	271.1631	3067		0	55.98	271.1637	1
266	4.19	20.71	519.0077	3048	320.8	2	61.58	1040.0299	2
267	3.383	24.08	446.1484	3031		0	56.35	446.149	1
268	5.482	19.85	243.1698	3021		0	60.65	243.1704	1
269	7.562	28.83	625.1748	2975		0	54.39	625.1753	1
270	4.26	17.66	265.03	2965		0	69.42	265.0305	1
271	6.196	16.19	189.0773	2962		0	52.97	189.0779	1
272	12.62	14.33	180.9731	2950		0	60.82	180.9736	1
273	6.093	24.32	449.1048	2911	193.5	1	55.37	450.1121	2
274	3.55	14.35	180.973	2894		0	56.31	180.9735	1
275	9.702	20.11	303.0389	2876	161.6	1	50.81	304.0462	2
276	14.819	13.23	154.9744	2876		0	62.94	154.9749	1
277	15.811	19.51	378.9161	2873		0	56.6	378.9166	1
278	10.974	19.82	285.039	2859		0	52.43	285.0396	1
279	4.594	23.75	447.147	2849		0	54.37	447.1476	1
280	9.843	27.93	545.1777	2821		0	65.09	545.1783	1
281	3.613	23.42	436.0837	2804		0	67.26	436.0842	1
282	10.533	17.57	304.9121	2801		0	67.97	304.9126	1
283	10.759	14.32	180.9731	2799	117.1	1	54.04	181.9804	2
284	15.992	22.77	353.1979	2789	182.4	1	91.75	354.2052	2
285	2.77	19.53	378.9157	2783		0	79.44	378.9163	1
286	15.917	14.31	180.9724	2776		0	63.48	180.9729	1
287	11.917	15.26	216.934	2758		0	50.95	216.9345	1
288	13.013	19.08	243.1592	2757		0	63.39	243.1597	1
289	15.274	14.33	180.973	2752		0	60.64	180.9735	1
290	4.279	23.73	413.1634	2747		0	50.14	413.164	1
291	14.062	14.33	180.9729	2694		0	59.71	180.9735	1
292	4.086	19.71	305.0163	2693		0	55.56	305.0169	1
293	6.753	23.63	576.6214	2674	366.9	2	55.77	1155.2573	2
294	8.107	21.68	407.023	2670		0	52.44	407.0236	1
295	11.809	15.73	189.0174	2659		0	61.34	189.018	1
296	4.105	19.7	305.0145	2641		0	88.53	305.0151	1
297	12.514	20.3	440.8855	2629		0	59.98	440.8861	1
298	3.802	22.22	423.0578	2606		0	68.41	423.0583	1
299	11.634	13.12	154.9745	2603		0	57.1	154.975	1
300	5.493	22.65	382.1106	2547	181	1	62.12	383.1179	2
301	15.476	19.5	378.9168	2541		0	78.21	378.9174	1
302	3.86	25.89	510.0502	2532	205.6	1	65.02	511.0575	2
303	12.802	14.32	180.9736	2524		0	52.04	180.9741	1
304	3.258	25.27	481.0948	2516		0	63.79	481.0953	1
305	5.954	23.3	588.1188	2501	361.7	2	53.82	1178.2522	2
306	8.16	14.32	180.9731	2485		0	60.35	180.9737	1
307	12.337	17.75	310.9275	2485		0	77.53	310.9281	1
308	12.229	14.43	191.946	2477		0	56.93	191.9466	1
309	7.896	17.69	304.9125	2475		0	70.69	304.9131	1
310	8.563	25.39	455.0931	2460	202.2	1	65.59	456.1003	1
311	4.085	19.97	477.0139	2456	309.3	2	52.28	956.0424	2
312	15.973	14.31	180.9728	2441		0	60.64	180.9733	1

313	5.01	25.34	514.9682	2425		0	69.37	514.9688	1
314	10.945	15.77	230.9552	2421		0	53.24	230.9557	1
315	10.642	15.84	230.9554	2416		0	59.62	230.956	1
316	10.856	17.8	304.9114	2407		0	56.04	304.9119	1
317	11.338	15.75	190.0205	2384		0	51.65	190.0211	1
318	8.569	20.45	317.03	2382		0	54.55	317.0305	1
319	2.326	18.88	319.0009	2367	151.2	1	65	320.0082	2
320	14.185	13.13	154.9746	2360		0	52.39	154.9751	1
321	4.142	22.82	1001.0747	2353	178.5	1	64.75	1002.082	2
322	9.02	18.16	214.1448	2351		0	55.84	214.1454	1
323	4.911	23.5	373.1109	2348	188	1	92.2	374.1182	2
324	15.023	13.21	154.973	2333		0	53.65	154.9735	1
325	4.127	16.97	219.0511	2327		0	63.16	219.0517	1
326	10.247	14.25	180.9727	2324	116.5	1	59.54	181.98	1
327	9.972	15.81	230.9548	2315		0	56.52	230.9554	1
328	13.434	15.23	218.9324	2273		0	58.29	218.9329	1
329	12.485	17.8	310.9278	2269		0	52.94	310.9283	1
330	3.79	14.33	180.9731	2222		0	54.02	180.9736	1
331	10.697	15.78	230.9538	2219		0	60.62	230.9543	1
332	4.06	19.91	466.0222	2188	308.5	2	94.68	934.059	2
333	4.938	20.19	294.123	2175		0	57.85	294.1236	1
334	4.952	19.35	271.1632	2172		0	55.85	271.1638	1
335	3.778	18.53	241.0323	2155		0	62.83	241.0328	1
336	7.797	23.19	407.0566	2151		0	59.1	407.0572	1
337	12.819	17.71	310.9307	2147		0	51.82	310.9313	1
338	5.706	24.49	402.1478	2132		0	61.69	402.1484	1
339	6.532	13.99	119.0481	2118		0	76.02	119.0487	1
340	11.487	14.21	180.9743	2107		0	67.21	180.9749	1
341	6.452	16.98	186.1112	2104		0	53.1	186.1117	1
342	12.494	14.44	191.9451	2104		0	52.93	191.9456	1
343	10.615	19.87	271.0603	2099		0	52.01	271.0608	1
344	9.995	19.55	378.916	2098		0	57.68	378.9166	1
345	6.507	16.66	197.0438	2091		0	53.42	197.0444	1
346	8.665	14.34	180.9726	2088		0	58.35	180.9731	1
347	8.647	14.32	180.9732	2068		0	70.68	180.9737	1
348	15.009	14.56	191.9451	2056		0	50.79	191.9457	1
349	4.229	21.57	312.0429	2042	173.5	1	71.72	313.0501	1
350	11.816	15.16	216.9358	2041	122.9	1	63.48	217.943	2
351	5.512	22.26	326.0558	2038		0	52.49	326.0564	1
352	3.085	21.14	390.9947	2033		0	61.18	390.9952	1
353	8.613	14.32	180.9739	2022		0	53.82	180.9745	1
354	8.471	20.43	318.0323	2020	163.9	1	59.84	319.0396	2
355	3.654	21.66	368.095	2014		0	50.16	368.0956	1
356	12.257	20.44	440.8863	2009		0	63.61	440.8869	1
357	5.267	26.04	481.0928	2002		0	62.79	481.0933	1
358	6.405	25.19	720.6583	2000		0	59.8	720.6589	1
359	10.411	15.83	230.954	1994		0	56.41	230.9545	1
360	5.394	14.32	180.9728	1988		0	58.61	180.9733	1
361	14.989	13.17	154.9737	1983		0	57.2	154.9743	1
362	5.969	23.67	427.0299	1956		0	60.32	427.0304	1
363	3.813	14.32	180.9732	1946		0	52.97	180.9737	1
364	12.551	17.7	310.9277	1933		0	75.13	310.9282	1
365	5.853	14.32	180.9727	1933		0	61.66	180.9733	1

366	15.207	13.12	154.975	1909		0	64.4	154.9755	1
367	10.474	15.78	230.9532	1901		0	51.96	230.9537	1
368	4.343	19.26	229.1545	1898		0	52.65	229.1551	1
369	7.339	17.66	304.9123	1884		0	56.71	304.9128	1
370	11.177	20.94	315.0487	1884		0	58.44	315.0493	1
371	13.888	14.41	180.9728	1869		0	60.65	180.9734	1
372	2.664	21.17	377.0025	1854		0	60.88	377.0031	1
373	11.159	18.36	274.9955	1848		0	60.42	274.996	1
374	10.002	14.44	191.945	1844		0	56.93	191.9455	1
375	11.271	17.44	246.9744	1815		0	92.78	246.975	1
376	6.128	19.13	289.0681	1810		0	78.92	289.0686	1
377	6.732	26.1	475.1795	1810		0	64.94	475.18	1
378	4.278	15.87	179.0341	1808		0	55.05	179.0346	1
379	3.493	19.34	291.0978	1767		0	61.55	291.0984	1
380	12.956	13.25	146.9603	1766		0	55.73	146.9609	1
381	13.942	15.22	218.9318	1763		0	51.07	218.9324	1
382	3.954	21.54	393.0459	1756		0	56.68	393.0464	1
383	2.256	18.64	312.985	1728		0	52.28	312.9856	1
384	8.533	23.13	360.2382	1712		0	64.02	360.2387	1
385	2.769	18.99	287.0333	1710		0	50.73	287.0339	1
386	3.008	22.72	345.078	1710	182.1	1	53.9	346.0853	1
387	4.42	27.97	543.2245	1698		0	75.23	543.225	1
388	4.34	28.2	617.1087	1694		0	51.15	617.1092	1
389	6.748	14.38	180.9726	1683		0	50.04	180.9731	1
390	13.237	18.17	248.9605	1667		0	54.82	248.961	1
391	12.378	17.73	310.928	1666		0	74.37	310.9286	1
392	11.786	15.69	189.0169	1664		0	71.05	189.0175	1
393	4.971	25.29	577.1286	1652		0	60.8	577.1292	1
394	3.692	20.84	305.0654	1652		0	73.43	305.0659	1
395	10.047	20.08	301.0339	1630		0	54.57	301.0344	1
396	3.037	19	291.0008	1621		0	60.18	291.0013	1
397	3.123	19.32	309.0192	1609		0	53.9	309.0197	1
398	15.119	13.2	154.9734	1608		0	70.8	154.974	1
399	2.563	19.6	378.9173	1606		0	70.26	378.9178	1
400	2.515	21.02	377.0012	1604		0	53.33	377.0018	1
401	3.122	20.88	354.0093	1591		0	72.65	354.0099	1
402	5.754	21.37	326.9993	1590		0	63.39	326.9998	1
403	13.883	13.24	154.9735	1567		0	77.82	154.974	1
404	4.978	15.48	163.0384	1566		0	62.64	163.039	1
405	13.624	13.22	154.9749	1560		0	50.74	154.9754	1
406	3.131	14.44	153.0184	1543		0	74.7	153.019	1
407	3.836	19.57	303.0028	1536		0	68.41	303.0034	1
408	11.297	17.45	191.0708	1505		0	56.01	191.0714	1
409	14.525	14.44	180.9723	1504		0	53.08	180.9728	1
410	11.141	17.45	248.9723	1503		0	88.99	248.9728	1
411	4.951	26.41	577.1358	1502	209.2	1	59.94	578.1431	1
412	6.371	25.1	502.0883	1501		0	59.85	502.0888	1
413	15.706	20.11	266.1512	1486		0	67.85	266.1517	1
414	3.741	18.45	241.0308	1485	149.6	1	61.8	242.0381	1
415	11.491	17.78	257.0038	1471		0	68.22	257.0043	1
416	14.225	13.22	154.9743	1467		0	74.38	154.9748	1
417	3.122	14.33	180.9725	1464		0	52.19	180.973	1
418	11.261	19.69	319.9776	1450		0	69.2	319.9781	1

419	7.731	23.44	451.101	1438		0	51.23	451.1016	1
420	15.969	22.01	311.1672	1436	177.1	1	66.63	312.1745	2
421	3.22	20.09	358.9876	1430		0	57.07	358.9882	1
422	4.828	13.81	149.0087	1428		0	78.41	149.0092	1
423	7.881	24.43	415.1955	1423		0	62.56	415.1961	1
424	4.565	22.57	427.0296	1400		0	51.14	427.0301	1
425	15.094	13.23	154.9726	1398		0	75.81	154.9732	1
426	7.934	18.55	241.1065	1398		0	68.83	241.107	1
427	11.147	19.74	257.0024	1385		0	58.9	257.0029	1
428	11.213	15.66	146.0304	1382		0	81.07	146.0309	1
429	5.399	20.93	357.1156	1378		0	56.69	357.1161	1
430	9.673	24.29	458.9883	1373		0	54.37	458.9888	1
431	4.79	21.91	355.0571	1361		0	53.64	355.0576	1
432	15.75	22.26	333.1328	1354		0	55.47	333.1334	1
433	11.309	22.75	454.9482	1340		0	50.76	454.9487	1
434	6.303	18.02	233.0425	1323	146.2	1	54.03	234.0498	2
435	14.941	20.92	452.9182	1307		0	58.32	452.9188	1
436	4.304	24.7	730.6398	1299		0	61.36	730.6404	1
437	4.797	13.93	149.0077	1284		0	60.1	149.0082	1
438	13.991	13.2	154.9737	1255		0	55.91	154.9742	1
439	11.699	15.69	189.016	1254		0	51.54	189.0165	1
440	4.531	17.64	259.0104	1249		0	63.61	259.011	1
441	3.855	19.61	303.0013	1242		0	73.84	303.0019	1
442	12.27	20	401.9235	1236		0	56.43	401.924	1
443	15.58	20.1	266.1493	1233		0	54.83	266.1498	1
444	4.391	18.67	197.0068	1210		0	51.92	197.0074	1
445	3.29	24.03	429.1575	1200		0	52.38	429.158	1
446	4.505	19.99	305.0158	1195		0	77.71	305.0163	1
447	5.746	20.79	333.0197	1183		0	61.32	333.0202	1
448	11.382	19.71	318.9717	1183		0	51.4	318.9722	1
449	6.318	23.43	353.0966	1175		0	52.11	353.0971	1
450	9.665	24.05	430.9893	1172		0	53.9	430.9899	1
451	5.628	20.96	486.0898	1142	325	2	55.51	974.1942	2
452	2.254	14.81	161.0469	1140	122.3	1	51.3	162.0542	2
453	12.381	15.77	189.0167	1131		0	71.1	189.0172	1
454	12.178	22.07	341.0624	1126		0	51.23	341.0629	1
455	13.489	24.15	361.163	1125		0	54.13	361.1636	1
456	2.217	20.21	279.0959	1125		0	61.05	279.0964	1
457	14.777	14.25	180.9741	1122		0	57.56	180.9746	1
458	2.006	18.29	232.0577	1120		0	51.88	232.0582	1
459	9.688	24.91	498.9766	1120		0	56.32	498.9771	1
460	2.103	18.3	232.058	1088		0	51.44	232.0586	1
461	13.766	17.91	310.9291	1085		0	69.61	310.9297	1
462	15.528	13.12	154.974	1076		0	70.62	154.9745	1
463	10.684	19.89	273.0755	1074		0	70.93	273.076	1
464	5.424	21.47	316.1829	1068		0	72.95	316.1835	1
465	4.054	20.42	277.1184	1052		0	57.62	277.1189	1
466	4.089	20.58	373.0053	1050		0	54.16	373.0058	1
467	9.732	13.84	158.9777	1049		0	54.4	158.9783	1
468	3.648	22.25	398.9985	1035		0	66.1	398.9991	1
469	4.326	23.41	462.9763	1032		0	53.92	462.9769	1
470	4.151	24.66	667.0508	1028		0	53.41	667.0513	1
471	12.985	21.48	345.1075	1014		0	60.89	345.1081	1

472	3.77	21.49	335.1311	1004		0	59.03	335.1316	1
473	5.016	25.24	487.1391	1001		0	51.29	487.1396	1
474	7.576	26.87	488.3074	973		0	54.68	488.308	1
475	4.511	17.87	243.0459	971		0	54.9	243.0465	1
476	8.904	20.47	317.0288	953		0	60.75	317.0294	1
477	2.804	21.17	390.9956	953		0	55.33	390.9962	1
478	4.872	19.97	295.0449	952		0	53.07	295.0454	1
479	13.044	17.79	310.9282	935		0	53.88	310.9288	1
480	11.46	14.32	161.0215	919		0	52.31	161.022	1
481	11.214	17.39	248.9721	905		0	55.21	248.9727	1
482	15.993	20.21	506.9522	897		0	53.77	506.9527	1
483	4.23	15.75	183.0294	891		0	54	183.0299	1
484	15.441	20.12	265.1471	877		0	50.83	265.1476	1
485	4.067	19.86	458.0283	866		0	51.05	458.0289	1
486	13.028	15.24	220.9289	857		0	59.98	220.9294	1
487	4.446	14.57	153.0184	857		0	60.61	153.019	1
488	5.954	21.74	397.021	847		0	50.39	397.0215	1
489	5.037	22.68	413.0132	832		0	52.79	413.0137	1
490	4.537	19.49	295.0078	822		0	54.81	295.0084	1
491	11.328	17.67	189.0159	783		0	50.72	189.0165	1
492	4.491	18.46	266.009	773		0	53	266.0096	1
493	8.104	21.89	413.0402	772		0	50.66	413.0408	1
494	3.88	18.76	303.0072	758		0	55.38	303.0078	1
495	12.9	19.02	300.9983	753		0	51.31	300.9989	1
496	4.461	22.28	391.1178	753		0	59.54	391.1184	1
497	4.542	27.68	581.1156	741		0	55.43	581.1161	1
498	11.152	27.23	604.98	726		0	51.15	604.9805	1
499	10.093	17.94	180.9743	716	147.8	1	53.89	181.9815	1
500	6.062	24.06	465.0063	707		0	55.12	465.0069	1
501	3.679	18.48	241.0324	706		0	57.37	241.033	1
502	12.031	15.75	189.0153	702		0	52.09	189.0158	1
503	11.695	16.01	112.9858	693		0	50.28	112.9863	1
504	13.581	15.04	220.9307	689		0	54.3	220.9313	1
505	3.815	19.04	229.1556	675		0	54.84	229.1561	1
506	13.161	22.92	556.8786	650		0	52.62	556.8792	1
507	5.635	25.92	487.1382	649		0	51.21	487.1388	1
508	11.644	17.79	234.0085	643		0	52.72	234.009	1
509	6.476	21.81	314.2017	617		0	52.28	314.2022	1
510	4.921	23.33	372.2138	606		0	51.82	372.2144	1
511	3.908	23.64	457.0953	588		0	51.26	457.0958	1
512	14.045	15.65	189.017	567		0	51.78	189.0176	1
513	13.219	13.65	166.9248	555		0	54.49	166.9254	1
514	10.993	17.36	174.9548	532		0	52.24	174.9554	1
515	12.505	13.67	161.9475	482		0	51.95	161.948	1
516	10.886	13.91	158.9786	469		0	50.36	158.9792	1
517	13.058	24.07	325.182	203		0	94.42	325.1825	1

D.2.2. LC-TOF

ID	RT	Mass	Abund	Score
1	11.185	190.0246	31198120	100
2	4.158	312.0481	8633019	100
3	4.545	176.0688	7340749	100
4	11.184	402.0301	6415990	100
5	5.177	290.0788	5620999	100
6	4.158	624.0962	5503637	100
7	6.401	198.0531	4010168	100
8	5.999	290.0791	3116831	100
9	4.998	296.0533	3086351	100
10	4.947	578.1424	2956368	100
11	9.68	302.0427	2584587	100
12	5.434	180.0426	2504387	100
13	4.415	130.0265	2030857	100
14	4.158	646.0781	1803084	100
15	5.803	578.1427	1730050	100
16	4.415	176.0692	1290159	100
18	4.546	374.1193	1146534	100
19	6.333	367.126	1077445	100
20	9.748	208.0739	969333	100
21	8.402	318.038	921391	100
22	7.513	626.1851	851969	100
23	11.185	614.0363	808863	100
24	4.017	316.116	793092	100
25	3.428	154.0634	769306	100
26	5.177	358.0664	747816	100
27	8.203	390.1315	742309	100
28	11.186	470.0176	741478	100
29	3.329	430.1685	735446	100
30	5.689	448.1583	681890	100
31	3.802	594.1374	672591	100
32	4.157	150.0169	667505	100
33	7.406	478.075	657846	100
34	3.153	157.0742	655387	97.6
35	9.796	228.0791	654647	100
36	6.226	428.0413	625168	100
37	6.507	164.0476	619282	100
38	7.152	436.1371	584659	100
39	5.999	358.0665	569959	100
40	4.416	374.119	564473	100
41	4.417	244.0561	539309	100
42	8.12	508.1217	533201	100
43	3.669	306.0739	530607	100
44	7.71	340.0796	521056	100
45	5.519	326.0639	515074	100
46	11.184	608.0192	504693	100
47	11.389	243.1838	484921	100
48	3.27	400.158	484909	100
49	4.812	296.0536	484186	100
50	3.703	220.0586	453251	100
51	6.312	166.0633	451919	100
52	3.059	154.0267	441848	100
53	2.945	144.0425	436516	100
54	4.158	180.0427	429719	100
55	3.837	488.0738	420717	100
56	4.307	617.1161	418603	100
57	11.105	316.0582	414076	100
58	2.942	162.0531	407612	80
59	11.186	464.0003	397860	100
60	6.006	154.0268	389981	100
61	7.409	626.1846	387635	100
63	4.093	220.0587	379302	100
64	4.999	364.0405	378210	100
65	5.003	444.1997	369989	100
67	11.184	275.002	341935	100
68	7.405	782.2055	340564	100
69	3.576	369.1061	334969	80
70	5.317	132.0788	329086	100
71	2.273	162.0532	326643	100
72	14.852	195.0899	324450	100
73	8.547	434.1209	317169	100
74	6.815	510.1371	297191	100
75	3.329	498.1557	291263	100
76	3.569	592.1099	288086	100
77	4.948	646.1302	284531	100
78	2.962	230.0407	280906	87
79	4.549	1097.0704	280270	100
80	3.516	280.1161	278403	100
81	3.169	230.0406	276447	100
82	5.803	646.13	275156	100
83	4.651	594.1372	264640	100
84	7.262	302.0046	262458	100
85	8.621	500.1468	260916	100
86	4.16	668.0598	260469	100
87	11.185	676.0066	255222	100
89	5.497	326.0998	251608	100
90	3.9	174.053	249388	80.1
91	11.236	325.9989	246731	100
92	9.678	370.0296	246603	100
93	4.571	244.0562	243263	80
95	6.464	866.2059	237572	100
96	4.926	294.1316	237031	100
97	6.334	435.1137	235323	100
98	7.471	510.231	234945	100

99	4.123	380.0355	233090	87
100	8.111	182.0583	232312	100
101	4.162	620.0646	232257	100
102	5.274	510.1373	232195	100
103	13.461	294.1831	231369	100
104	8.081	782.2061	231021	100
105	5.505	866.2054	228284	100
106	11.184	820.025	225947	100
107	8.079	452.1106	225866	100
108	6.788	508.1215	225416	100
109	4.232	176.0687	225011	100
110	11.185	146.0346	218989	100
111	7.251	168.0408	217138	100
112	3.513	386.1425	214661	100
113	9.747	332.0533	213027	100
114	8.091	188.1051	212255	100
116	3.14	220.0586	208273	100
117	6.179	190.0843	207980	100
118	3.466	231.0204	207717	100
119	4.546	572.1689	207701	100
120	7.789	340.0795	207536	100
121	4.16	628.1071	207208	80
122	7.426	596.1738	203424	100
124	4.018	384.103	198688	100
125	8.202	458.1185	198054	100
126	5.177	404.0716	197802	100
127	5.738	296.1474	196728	100
129	5.689	516.1452	193518	100
130	3.722	866.2055	192164	87
131	5.813	326.1	191566	100
132	5.998	336.0844	191446	100
133	11.252	192.079	189890	100
134	5.751	432.1994	183738	100
136	3.707	358.0867	181400	100
137	4.119	594.1372	181285	100
138	5.264	414.0256	179466	100
139	5.178	426.0535	179394	100
140	11.185	682.0232	178191	100
141	4.43	702.1118	175600	100
142	8.966	276.0998	173997	100
144	4.206	182.0582	173007	100
145	7.707	354.1315	169918	100
146	6.423	187.1212	169774	100
147	9.466	546.1887	169209	100
148	6.573	578.1417	168638	100
149	4.547	396.1007	165707	100
150	11.23	319.982	165440	100
151	3.836	510.0551	164903	100

152	7.048	205.0743	164517	100
153	4.203	402.0172	163830	96.7
154	7.526	450.1158	161784	100
155	5.602	866.206	161557	95.7
156	2.951	118.0632	161285	100
157	4.089	176.0688	159981	100
158	3.42	316.0794	159269	100
159	4.307	639.098	158717	100
160	4.774	244.056	158678	100
161	11.375	330.2405	156683	100
162	7.766	364.0791	156019	100
163	7.406	500.0563	155592	100
164	10.901	286.0478	155204	100
165	5.898	1070.2692	154900	100
166	8.852	228.0789	154783	100
167	6.044	428.1894	154412	100
168	4.085	244.0561	153310	100
169	5.177	336.0843	153280	100
170	9.797	274.0843	152692	100
171	7.151	504.1242	152203	100
172	4.804	414.1739	150892	100
173	3.348	658.0988	150776	87
174	4.187	668.0601	150190	87
175	4.416	306.0259	150106	98.2
176	5.303	316.1157	149935	100
177	4.52	244.056	149131	87
178	8.241	640.1999	147842	100
179	7.711	408.0666	143256	100
180	2.945	692.1747	143004	100
181	4.158	662.045	142300	80
182	5.857	512.1524	141269	100
184	5.001	386.0223	140671	100
185	8.203	436.1364	139906	100
186	4.038	634.1202	139541	100
187	7.514	648.1664	139399	100
188	6.412	1070.268	139398	100
189	5.434	248.0301	138293	100
190	11.143	325.9989	138211	100
191	5.872	242.1267	137401	100
192	11.184	418.004	135069	100
193	5.177	420.037	134669	100
194	6.401	266.0405	134457	100
195	9.679	416.0351	134001	100
196	11.189	531.9878	133522	89.7
197	5.449	448.1578	133134	100
198	6.31	234.0503	129109	100
199	4.126	532.1059	128834	100
200	5.999	426.0536	128176	100

201	11.184	247.983	125187	100	251	4.118	112.0162	99252	100
202	5.997	404.0716	123746	100	252	6.404	312.0458	99175	100
204	5.176	326.0555	122998	100	253	4.192	396.0004	98472	87
205	5.945	320.053	122100	100	254	7.335	204.0999	97502	100
206	4.968	306.0739	121820	100	256	6.812	510.2311	96631	100
207	8.967	230.0945	120580	100	257	4.018	430.1082	96443	100
208	11.184	826.0415	120247	100	258	3.8	662.1243	96069	100
209	4.932	214.0458	119803	100	259	5.326	158.058	95978	100
210	6.001	444.1057	118745	100	260	8.122	576.1089	95547	100
211	5.52	394.051	118134	100	261	3.167	298.0274	95347	99.4
212	5.246	326.101	116718	97	262	4.813	364.0404	94497	100
213	5.315	200.0663	116455	100	263	5.212	132.0788	93396	100
214	3.866	444.1841	116277	100	264	5.119	686.1303	93209	100
215	4.415	1097.0704	116262	100	265	5.69	402.1523	92570	100
216	5.417	428.1892	115140	100	266	3.669	374.0612	92400	100
218	11.388	311.1706	114291	100	267	6.094	450.1158	92115	100
219	5.618	488.1528	114209	83.9	268	5.999	326.0557	91690	100
220	7.513	694.1718	113911	100	269	11.244	387.9693	91435	100
221	6.217	496.0285	112948	93.1	270	10.469	906.2663	91428	100
222	7.485	494.1056	112105	100	271	6.095	488.153	91391	100
223	5.852	866.2059	111738	100	272	4.415	572.1693	91301	100
224	4.132	334.0303	111507	84.7	273	7.403	850.1925	91171	96.1
225	3.655	162.0891	111305	100	274	6.69	518.1578	91154	100
226	8.402	386.0251	110925	100	275	2.94	359.9981	91114	94.5
227	4.154	695.1554	110868	100	276	8.547	502.1083	90861	100
228	3.577	437.0932	110707	100	277	6.503	738.1466	90607	100
229	10.763	656.4497	109924	100	278	11.184	888.0117	90547	100
230	5.016	166.0271	107544	100	279	7.078	782.2053	90462	100
231	4.162	622.0806	106544	100	280	3.719	620.0553	89317	88.7
232	3.329	384.163	106261	100	281	13.745	357.2509	87328	100
233	2.943	292.0108	105125	99.5	282	5.059	294.1314	87269	100
234	6.729	494.0694	104819	100	283	6.63	466.1105	87065	100
235	5.353	418.1472	104547	100	284	6.029	488.153	85862	100
236	9.823	546.1885	103442	100	285	3.515	348.1031	85479	100
237	6.752	560.1159	103367	100	286	5.005	512.1867	85204	100
238	5.176	353.0748	101985	100	287	4.153	383.1073	85161	100
239	8.522	324.0845	101932	100	288	5.379	686.1305	84807	100
240	3.704	288.0454	101156	100	289	3.268	468.1451	84532	100
241	4.19	184.0373	100353	100	290	4.347	230.1634	84339	100
242	5.998	420.037	100201	100	291	6.023	430.2199	83988	100
243	4.449	360.1055	99938	86.4	292	6.553	276.1107	83753	100
244	9.679	438.017	99722	100	293	5.947	194.0206	83353	99.9
245	6.354	442.2045	99626	100	294	7.309	304.0584	83313	100
246	4.119	554.0883	99620	100	295	8.302	640.2004	83262	80
247	4.999	614.0888	99530	100	296	3.78	151.0272	83067	100
248	4.546	566.1521	99368	100	297	8.134	244.1313	83060	100
249	5.057	182.058	99315	100	298	5.803	668.112	82988	100
250	4.415	442.1062	99276	100	299	8.478	580.1789	82300	100

300	5.27	1086.2628	81536	96.6

D.3. Blaufränkisch-Zweigelt

D.3.1. LC-IM-(Q)TOF

Feature	RT	DT	m/z	Abund	Ω [$\AA^2$]	Z	Quality	Mass	Ions
1	11.19	15.77	189.0167	1074218	129.1	1	100	190.0239	
2	11.186	23.12	401.0211	778749	184.5	1	99.35	402.0284	
3	5.186	19.17	289.07	740680	154.2	1	100	290.0773	
4	6.002	19.16	289.0691	609460	154.1	1	100	290.0764	
5	6.401	16.7	197.0452	397381	136.6	1	75	198.0525	
6	4.955	27.54	577.1326	380666	218.3	1	100	578.1399	
7	5.807	27.71	577.1315	288583	219.7	1	100	578.1388	
8	4.548	15.49	175.0607	246901	127.4	1	100	176.068	
9	9.681	20.08	301.0344	212618	161.4	1	100	302.0417	
10	6.098	19.6	291.0854	164542	157.7	1	100	292.0927	
11	8.402	20.42	317.0289	151322	163.9	1	100	318.0362	
12	4.167	27.66	623.0889	145118	218.9	1	100	624.0962	
13	5.189	21.28	357.0571	141902	170.2	1	74.43	358.0644	
14	7.409	25.28	477.0641	137423	201	1	100	478.0713	
15	4.55	23.34	373.1101	135913	186.7	1	100	374.1174	
16	4.169	19.67	311.0401	134910	157.8	1	80.22	312.0473	
17	6.333	22.44	366.1177	134102	179.5	1	100	367.125	
18	11.155	17.75	257.003	120458	143.3	1	54.06	258.0103	
19	4.175	20.04	333.0219	118218	160.4	1	89.16	334.0292	
20	4.168	21.54	311.0408	116464	173.2	1	99.46	312.0481	
21	5.44	15.82	179.034	116185	129.9	1	100	180.0413	
22	7.556	27.15	497.3312	112142	216	1	97.76	498.3385	
23	5.999	21.3	357.0567	111356	170.3	1	100	358.0639	
24	8.202	22.42	389.1221	111053	179	1	100	390.1293	
25	3.682	19.59	305.0652	109149	157.3	1	73.42	306.0724	
26	5.004	20.98	295.044	97444	169	1	97.52	296.0512	
27	9.748	17.77	207.0651	81421	145.2	1	94.31	208.0724	
28	5.068	27.35	577.1323	72169	216.8	1	66.07	578.1396	
29	4.026	21	315.108	71918	168.7	1	56.28	316.1153	
30	5.005	24.16	443.1899	71777	192.4	1	100	444.1972	
31	4.165	29.44	645.0719	70393	233.1	1	98.28	646.0792	
32	3.592	21.63	368.0974	69829	172.9	1	94.15	369.1047	
33	4.313	28.19	616.1068	67210	223.2	1	100	617.1141	
34	5.185	27.28	579.1477	67052	216.2	1	74.75	580.155	
35	11.39	19.34	242.1755	64841	156.9	1	100	243.1828	
36	3.822	27.7	593.1282	63528	219.5	1	98.95	594.1355	
37	11.242	19.63	318.9723	56027	157.3	1	95.37	319.9796	
38	11.177	18.34	273.9934	55703		0	68.13	273.994	
39	3.546	22.42	385.1343	51951	179	1	89.4	386.1416	
40	3.854	25.15	487.0641	51943	199.9	1	83.39	488.0714	
41	11.216	24.54	469.0089	50591	195.2	1	54.11	470.0162	
42	7.087	27.26	497.3332	48558	216.9	1	95	498.3404	
43	7.266	19.02	300.997	44427	152.7	1	77.82	302.0043	
44	3.536	19.46	279.1075	43082	156.9	1	84.97	280.1148	
45	7.511	28.71	625.1728	43028	227.3	1	92.53	626.18	
46	3.321	23.22	399.1482	42838		0	70.88	399.1487	
47	6.815	26.89	509.129	42663	213.7	1	73.17	510.1363	

48	4.58	17.66	265.0295	42384	142.3	1	63.18	266.0368
49	7.525	24.3	449.1063	42373		0	57.51	449.1068
50	3.443	20.99	315.0708	42111	168.6	1	78.46	316.0781
51	6.097	20.47	313.0677	41034	164.3	1	98.66	314.0749
52	4.976	19.59	305.0638	40153	157.3	1	100	306.0711
53	2.962	22.7	345.0795	39828	182	1	96.52	346.0867
54	11.147	19.63	318.9727	39390	157.4	1	79.99	319.98
55	4.928	20.04	293.1223	39020	161.3	1	99.71	294.1296
56	4.549	22.13	395.093	38987	176.5	1	71.89	396.1002
57	5.503	22.3	325.0907	36618	179.1	1	89.27	326.098
58	5.694	24.84	447.1487	35698		0	79.99	447.1493
59	6.94	22.49	397.0587	35156		0	79.99	397.0592
60	3.187	22.39	345.0794	34904	179.5	1	80.22	346.0867
61	11.182	26.25	401.0206	34567	210	1	50.85	402.0278
62	9.799	19.06	227.0704	32913		0	73.15	227.071
63	5.695	24.54	401.1435	31448	196.1	1	76.68	402.1507
64	6.776	25.29	479.0805	31313	201.1	1	96.99	480.0878
65	8.118	26.84	507.1124	30992	213.4	1	67.33	508.1197
66	4.66	27.84	593.1297	30098	220.6	1	100	594.137
67	11.246	21.21	386.9598	29476	169.1	1	79.28	387.9671
68	7.41	25.75	499.0459	29318	204.6	1	66.57	500.0531
69	8.198	24.03	457.1093	28724	191.1	1	100	458.1166
70	6.576	27.75	577.1316	26537		0	70.67	577.1322
71	5.418	22.34	397.0583	26147	178.2	1	92.69	398.0656
72	3.698	18.26	243.0504	25706	147.9	1	74.11	244.0576
73	6.335	24.15	434.104	24070	192.4	1	95.32	435.1112
74	4.424	14.66	153.0194	23887		0	69.91	153.0199
75	3.724	21.34	357.078	22988	170.7	1	87.8	358.0853
76	4.423	23.07	351.0678	22157	185	1	78.64	352.075
77	5.718	22.31	397.0581	22086	177.9	1	100	398.0654
78	6.049	21.74	576.1228	21544	337	2	55.71	1154.2602
79	8.09	16.66	187.098	20180	136.7	1	69.42	188.1053
80	5.996	22.38	419.0273	20161		0	54.17	419.0278
81	5.299	22.17	397.0588	19225	176.8	1	93.37	398.0661
82	4.548	27.4	571.1614	19163	217.2	1	75	572.1687
83	5.817	22.24	325.0911	18551		0	58.9	325.0916
84	9.748	21.25	331.0448	18531	170.4	1	54.35	332.0521
85	11.104	21.03	315.0499	18497		0	70.76	315.0504
86	6.738	23.54	576.1232	18411	186	1	62.49	577.1305
87	4.104	16.98	219.0509	17438		0	51.29	219.0515
88	6.635	24.44	465.1018	17249	194.4	1	79.34	466.109
89	8.093	17.02	209.0791	17066		0	72.67	209.0796
90	3.857	25.87	509.0463	16762		0	51.79	509.0469
91	7.701	23.79	353.122	16160	190.8	1	71.21	354.1293
92	5.391	23.85	451.1224	16007	189.7	1	80.39	452.1297
93	5.683	21.53	576.1241	15948	333.7	2	61.71	1154.2628
94	6.79	26.71	507.1129	15929	212.3	1	59.72	508.1202
95	7.557	27.57	514.3204	15840	219.1	1	60.85	515.3276
96	7.766	22.54	363.0702	15369	180.4	1	73.07	364.0775
97	11.177	29.83	607.0087	15260		0	66.6	607.0092
98	11.138	21.22	386.9605	14984		0	72.33	386.961
99	4.184	13.87	149.0093	14615		0	53.77	149.0098
100	5.756	24.94	431.1892	14544	198.9	1	80.12	432.1965

101	7.486	25.98	493.0947	14164	206.5	1	72.1	494.1019	
102	8.546	23.96	433.1147	13378	190.9	1	52.01	434.122	
103	5.202	22.43	419.0277	13334		0	53.21	419.0282	
104	5.193	20.6	289.0707	12558	166	1	54.08	290.0779	
105	5.009	22.42	363.0307	12416	179.4	1	80.01	364.038	
106	5.456	25.17	447.1483	12358		0	64.79	447.1488	
107	5.172	20.59	289.0705	12156	165.9	1	54.57	290.0778	
108	5.167	21.35	358.0601	11851	170.7	1	70.01	359.0674	
109	4.052	19.98	315.1079	11624	160.3	1	66.25	316.1152	
110	4.553	26.87	565.1446	11529	213	1	94.87	566.1519	
111	3.538	21.81	347.0942	11375	174.7	1	80.59	348.1015	2
112	5.875	19.39	241.1175	11317	157.4	1	54.92	242.1248	2
113	4.029	24.15	451.0805	11158		0	64.31	451.0811	1
114	7.312	20.09	303.0493	11008	161.4	1	65.76	304.0566	2
115	5.384	29.7	685.1209	10959		0	54.62	685.1214	1
116	10.762	22.09	327.2157	10876		0	59.62	327.2162	1
117	4.514	17.63	265.0291	10835	142.1	1	54.86	266.0364	1
118	7.044	18.54	272.0536	10682	149.4	1	54.76	273.0609	2
119	2.993	20.51	358.9906	10580		0	63.63	358.9911	1
120	6.011	20.59	289.0705	10573	165.9	1	58.43	290.0778	2
121	3.796	21.51	331.1016	10476		0	51.83	331.1022	1
122	5.061	20.08	293.1221	10233		0	60.8	293.1226	1
123	6.726	25.72	493.0603	10043		0	83.81	493.0608	1
124	11.255	22.68	454.947	9872		0	57.47	454.9476	1
125	10.219	14.31	180.9729	9747		0	51.97	180.9735	1
126	5.989	20.56	289.0702	9581		0	55.18	289.0707	1
127	4.199	15.65	183.0296	9549		0	86.01	183.0301	1
128	4.095	18.51	243.048	9168		0	53.04	243.0485	1
129	2.145	22.19	413.0687	8936		0	59.9	413.0692	1
130	8.061	19.89	287.1484	8773	160.2	1	60	288.1557	2
131	3.679	21.84	373.0526	8200		0	52.73	373.0532	1
132	4.54	22.51	411.0583	8191	179.4	1	57.03	412.0656	2
133	3.796	20.66	299.0762	7392	166.2	1	99.99	300.0835	2
134	3.597	22.74	436.0847	7369	180.9	1	60.88	437.092	1
135	15.965	22.82	353.1995	7323		0	59.87	353.2	1
136	8.492	23.81	435.1282	7320		0	50.87	435.1288	1
137	4.132	21.44	333.0219	7266		0	53.03	333.0225	1
138	4.104	19.13	309.019	7261		0	50.62	309.0195	1
139	6.096	22.18	381.0542	7094		0	79.23	381.0548	1
140	4.536	22.38	417.074	7089		0	59.29	417.0746	1
141	3.707	19.56	306.0686	7053	157	1	87.13	307.0759	2
142	6.093	23.93	487.1416	6904		0	60.37	487.1421	1
143	15.765	20.03	265.1467	6797	161.9	1	52.19	266.154	2
144	6.501	15.5	163.0392	6525		0	54.42	163.0397	1
145	4.777	18.13	243.0469	6457		0	54.94	243.0474	1
146	5.841	29.91	685.1179	6440	236.6	1	60.82	686.1251	2
147	8.096	16.36	181.0506	6322	134.4	1	55.06	182.0579	2
148	4.133	23.3	462.9785	6248		0	52.62	462.9791	1
149	6.029	24.01	487.1431	6241	190.6	1	77.15	488.1504	2
150	8.202	25.66	525.0951	6224		0	52.34	525.0956	1
151	3.599	23.82	458.0673	6208		0	61.33	458.0679	1
152	8.889	14.31	180.9728	6200		0	55.8	180.9733	1
153	3.665	19.5	279.1078	6172		0	75.25	279.1083	1

154	9.524	14.32	180.9744	5946	117.1	1	60.02	181.9817	1
155	11.147	25.95	530.9785	5934	205.9	1	53.89	531.9857	2
156	4.315	25.66	495.1116	5842		0	51.18	495.1121	1
157	6.111	22.67	576.1248	5782	179	1	58.49	577.1321	2
158	6.696	22.63	347.1158	5769		0	62.95	347.1163	1
159	11.255	15.8	190.0189	5687	129.2	1	60	191.0262	2
160	4.21	16.89	181.052	5635		0	54.84	181.0526	1
161	11.133	22.7	454.9478	5545		0	77.63	454.9484	1
162	14.925	14.32	180.973	5497		0	66.83	180.9736	1
163	5.819	19.98	265.0707	5412		0	58.76	265.0713	1
164	3.747	21.33	357.0775	5386		0	52.34	357.0781	1
165	6.52	15.51	163.0388	5269		0	69.27	163.0394	1
166	4.428	16.69	129.0193	5261	140.9	1	61.31	130.0266	1
167	11.469	14.32	180.9728	5242		0	61.8	180.9733	1
168	4.054	28.57	633.1111	5179		0	76.11	633.1117	1
169	9.954	14.32	180.9732	5153		0	56.54	180.9737	1
170	5.438	14.24	135.0445	5151	119.1	1	52.73	136.0518	1
171	6.751	28.56	559.1056	5005		0	52.34	559.1062	1
172	4.183	20.67	519.0115	4918	320.3	2	68.54	1040.0376	2
173	2.024	19.62	294.0279	4899		0	51.97	294.0285	1
174	5.406	15.24	177.0187	4881		0	80.32	177.0192	1
175	4.834	20.05	295.0432	4873		0	50.04	295.0438	1
176	3.744	14.31	180.9727	4738		0	55.6	180.9733	1
177	6.14	19.12	289.0695	4695		0	63.68	289.0701	1
178	4.203	25.3	515.0806	4654		0	56.76	515.0812	1
179	5.498	20	265.0704	4595	161.7	1	55.18	266.0777	2
180	4.029	22.93	399.059	4590	182.9	1	79.36	400.0662	1
181	4.921	18.91	275.0068	4512		0	56.53	275.0074	1
182	6.177	16.18	189.077	4481		0	78.26	189.0775	1
183	10.842	14.35	180.9731	4467		0	61.44	180.9737	1
184	11.171	15.88	191.0209	4301		0	58.87	191.0215	1
185	13.42	17.68	304.9131	4212	141.5	1	52.32	305.9204	2
186	5.041	17.34	254.9866	4204		0	65.04	254.9871	1
187	11.223	18.74	298.9913	4122		0	62.76	298.9919	1
188	11.624	14.34	180.9728	4090		0	65.46	180.9734	1
189	6.326	16.17	165.0561	4085		0	62.42	165.0566	1
190	7.387	27.85	577.1307	4079	220.8	1	52.97	578.138	2
191	14.022	14.3	180.9735	4008		0	64	180.9741	1
192	4.57	16.07	219.0252	4001		0	57.26	219.0257	1
193	3.251	25.21	481.0944	3974		0	70.33	481.095	1
194	14.416	14.32	180.9733	3916		0	66.36	180.9738	1
195	6.309	19.44	295.012	3883		0	51.97	295.0126	1
196	6.773	14.33	180.9731	3836		0	51.37	180.9737	1
197	5.003	22.3	295.0431	3802	179.9	1	57.69	296.0504	1
198	2.942	21.16	301.09	3756	170.3	1	52.87	302.0973	2
199	8.284	20.01	287.056	3735		0	68.25	287.0565	1
200	4.457	21.01	323.1332	3669	168.6	1	57.25	324.1405	2
201	4.573	22.04	389.0745	3666		0	61.06	389.0751	1
202	2.192	14.32	180.9731	3664		0	63.02	180.9737	1
203	5.085	20.99	295.0451	3645		0	58.56	295.0456	1
204	8.825	14.31	180.973	3629		0	62.86	180.9736	1
205	2.312	17.06	251.0151	3572	137.7	1	58.92	252.0224	1
206	12.276	14.34	180.9731	3455		0	59.37	180.9736	1

207	11.801	15.74	189.0158	3366		0	83.5	189.0164	1
208	10.011	15.83	230.9552	3364		0	93.68	230.9557	1
209	11.694	15.77	189.0163	3361		0	56.79	189.0169	1
210	13.792	14.35	180.9731	3330		0	52.8	180.9736	1
211	4.188	19.93	704.9995	3307	156.2	1	58.17	706.0068	2
212	3.463	15.25	153.0554	3296		0	59.8	153.0559	1
213	5.575	25.85	487.1433	3294		0	50.07	487.1438	1
214	11.132	24.53	522.9338	3250		0	65.46	522.9344	1
215	3.68	14.33	180.9733	3179		0	62.3	180.9739	1
216	15.916	15.15	216.9342	3174		0	50	216.9348	1
217	5.691	22.1	587.6188	3109		0	61.2	587.6194	1
218	13.49	15.09	218.9319	3103		0	58.15	218.9324	1
219	5.147	23.59	584.1215	3058	366.2	2	77.9	1170.2576	2
220	6.743	16.51	195.0634	3042		0	57.02	195.064	1
221	14.367	14.31	180.9736	3027		0	54.32	180.9742	1
222	4.401	22.46	440.9928	3006		0	61.24	440.9934	1
223	3.988	22.05	369.0265	2996		0	64.16	369.027	1
224	15.006	20.87	446.9029	2958		0	66.48	446.9035	1
225	15.987	21.5	309.1708	2938	172.9	1	56.72	310.1781	2
226	11.795	19.55	378.916	2915		0	76.21	378.9165	1
227	10.176	17.8	310.9282	2908		0	51.43	310.9287	1
228	11.853	18.79	251.1258	2870		0	92.53	251.1264	1
229	4.804	13.83	149.007	2859		0	96.57	149.0075	1
230	15.476	19.54	378.9157	2849		0	71.52	378.9162	1
231	10.561	19.75	271.0597	2839		0	51.99	271.0602	1
232	8.336	23.29	419.1303	2839	185.6	1	64.92	420.1376	2
233	13.844	14.28	180.9731	2821		0	60.19	180.9736	1
234	12.872	15.16	218.9318	2800		0	62.93	218.9323	1
235	11.718	15.16	216.9338	2785		0	67.77	216.9344	1
236	10.701	22.01	327.2153	2735		0	67.35	327.2158	1
237	2.091	19.6	294.0285	2703		0	67.23	294.0291	1
238	3.312	14.32	180.973	2699		0	61.66	180.9735	1
239	15.675	15.09	216.9344	2603		0	74.89	216.9349	1
240	2.901	14.86	169.0147	2573		0	76.37	169.0153	1
241	5.755	19.59	265.0309	2570		0	65.67	265.0314	1
242	8.197	25.39	519.0789	2565		0	74.24	519.0795	1
243	8.487	20.43	317.0295	2540		0	56.34	317.0301	1
244	14.701	14.55	191.9456	2538		0	60.48	191.9461	1
245	10.544	14.28	180.9725	2424		0	52.68	180.9731	1
246	4.449	21.44	329.0244	2411	172	1	79.73	330.0317	2
247	15.513	17.86	310.9288	2407		0	83.92	310.9294	1
248	6.533	20.26	347.0741	2376	162	1	87.78	348.0814	2
249	15.624	20.08	266.1494	2372		0	78.06	266.1499	1
250	14.964	14.29	180.9743	2367		0	72.16	180.9749	1
251	5.615	25.92	477.0991	2364		0	50.97	477.0997	1
252	7.06	20.37	334.0248	2356		0	70.72	334.0253	1
253	12.568	14.33	180.973	2353		0	57.94	180.9735	1
254	5.059	16.18	181.0498	2352		0	80.17	181.0504	1
255	6.397	20.31	280.995	2350		0	51.18	280.9956	1
256	5.81	24.59	577.1302	2349	194.5	1	69.63	578.1375	1
257	7.751	19.21	261.1328	2344		0	61.71	261.1334	1
258	11.586	15.75	189.0151	2342		0	69.71	189.0156	1
259	15.437	14.33	180.9725	2338		0	88.66	180.9731	1

260	11.801	15.9	174.9554	2328		0	51.62	174.9559	1
261	14.075	19.59	378.9151	2319		0	54.22	378.9157	1
262	5.637	17.58	304.9124	2313		0	81.11	304.9129	1
263	6.726	16.38	195.0632	2281		0	83.7	195.0638	1
264	8.098	20.42	345.0516	2278		0	50.87	345.0521	1
265	15.439	13.19	119.0354	2278		0	50.59	119.036	1
266	12.989	19.54	378.9157	2261		0	58.71	378.9162	1
267	4.514	16.01	219.0249	2249		0	75.64	219.0254	1
268	4.407	24.33	441.0971	2210	193.8	1	71.34	442.1044	2
269	7.344	25.04	419.1679	2160		0	62.55	419.1684	1
270	10.674	14.32	180.9728	2147		0	51.84	180.9734	1
271	2.263	20.28	380.9703	2145		0	55.77	380.9708	1
272	2.201	20.28	279.0961	2143		0	57.22	279.0967	1
273	11.231	15.78	191.0216	2139		0	59.71	191.0221	1
274	15.255	14.4	180.9738	2128		0	50.43	180.9744	1
275	3.466	14.32	180.9725	2125		0	55.37	180.973	1
276	3.557	19.42	280.1108	2117		0	67.97	280.1114	1
277	6.555	20.84	319.0783	2111	167.3	1	50.32	320.0856	2
278	14.898	15.19	216.9341	2107		0	50.69	216.9347	1
279	4.421	14.35	129.0191	2100	120.5	1	51.78	130.0264	1
280	15.983	22.59	325.1822	2074		0	50.34	325.1828	1
281	3.697	21.96	438.9759	2056		0	53.5	438.9765	1
282	10.943	20.81	475.1302	2025		0	57.72	475.1307	1
283	14.989	14.44	191.9453	2017		0	55.22	191.9458	1
284	6.831	18.69	247.1551	2007		0	52.6	247.1557	1
285	10.91	20.85	452.1253	2001		0	61.23	452.1258	1
286	7.834	14.31	180.9745	1980		0	59.18	180.975	1
287	10.235	15.82	230.9552	1977		0	50.08	230.9558	1
288	15.334	15.27	216.934	1972		0	68.07	216.9345	1
289	6.114	20.44	314.072	1951		0	64.98	314.0725	1
290	4.95	26.12	577.1285	1925	206.8	1	68.9	578.1358	1
291	3.226	15.8	156.0659	1913		0	56.5	156.0665	1
292	4.034	24.01	399.0586	1911	191.7	1	66.21	400.0658	1
293	15.341	14.36	180.9726	1908		0	50.66	180.9731	1
294	15.385	14.44	191.9452	1901		0	69.64	191.9458	1
295	2.95	21.18	390.9978	1901	168.8	1	73.1	392.005	2
296	10.631	15.91	174.9551	1900		0	50.5	174.9557	1
297	9.425	17.2	201.112	1893	140.6	1	75.72	202.1193	2
298	9.732	15.82	230.9549	1890		0	62.37	230.9555	1
299	4.847	22.14	576.1215	1885		0	51.1	576.1221	1
300	11.187	14.32	162.0242	1877		0	90.21	162.0247	1
301	4.908	21.66	410.9807	1864		0	66.63	410.9812	1
302	10.161	15.83	230.9528	1850		0	56.35	230.9534	1
303	12.956	15.16	216.9344	1846		0	57.23	216.935	1
304	13.463	19.49	378.9173	1844		0	57.17	378.9178	1
305	11.31	19.78	257.0012	1838		0	56.14	257.0017	1
306	4.189	22.23	394.9959	1829		0	57.86	394.9964	1
307	5.067	15.46	183.0289	1825		0	53.02	183.0295	1
308	14.769	15.16	216.9337	1816		0	67.71	216.9342	1
309	5.297	17.68	304.9132	1811		0	54.53	304.9137	1
310	15	14.3	180.9737	1794		0	52.66	180.9743	1
311	5.402	17.68	304.9114	1791		0	73.29	304.9119	1
312	10.438	17.73	310.9272	1789		0	50.16	310.9278	1

313	15.572	15.1	216.9333	1786		0	59.59	216.9339	1
314	5.71	21.53	576.6239	1779	333.7	2	50.81	1155.2623	2
315	11.66	15.76	189.016	1778		0	64.04	189.0165	1
316	2.269	20.93	446.9027	1754		0	65.51	446.9032	1
317	5.342	17.71	304.9109	1751		0	50.16	304.9114	1
318	13.102	19.62	378.9174	1745		0	52.19	378.9179	1
319	4.176	16.8	344.0152	1738	133.7	1	62.14	345.0225	1
320	12.288	15.12	216.9345	1737		0	57.61	216.9351	1
321	9.697	20.05	303.0386	1736		0	58.46	303.0392	1
322	12.823	17.76	242.9424	1735		0	56.75	242.9429	1
323	11.506	17.69	257.0024	1733		0	51.41	257.0029	1
324	2.925	17.56	247.0125	1733		0	64.2	247.013	1
325	11.569	15.65	189.0161	1731		0	60.29	189.0166	1
326	11.99	14.32	180.9726	1726		0	55.57	180.9731	1
327	3.988	14.27	180.9725	1722		0	55.23	180.973	1
328	6.233	24.68	720.6537	1720		0	51.74	720.6542	1
329	7.801	28.43	551.1378	1718		0	61.7	551.1384	1
330	2.732	14.32	180.9733	1717		0	66.35	180.9738	1
331	14.472	15.25	218.9323	1707		0	54.34	218.9329	1
332	9.547	15.77	230.9545	1697		0	76.1	230.9551	1
333	2.215	18.94	244.1282	1692		0	76.9	244.1288	1
334	5.33	16.89	199.0589	1687		0	70.65	199.0595	1
335	5.414	14.25	135.0449	1681		0	54.59	135.0455	1
336	14.646	17.72	310.9286	1679		0	83.77	310.9292	1
337	10.036	15.77	230.9545	1666		0	63.35	230.955	1
338	15.368	19.49	378.9168	1657		0	59.97	378.9173	1
339	7.72	23.83	354.1259	1629		0	50.04	354.1264	1
340	3.404	15.35	153.055	1628		0	78.73	153.0556	1
341	5.339	21.59	584.6225	1606		0	56.75	584.6231	1
342	11.205	13.57	129.015	1604		0	67.67	129.0155	1
343	4.558	17.83	243.0466	1585		0	86.67	243.0472	1
344	6.215	23.35	384.2475	1580		0	58.75	384.248	1
345	14.986	16.86	194.0819	1567		0	68.71	194.0825	1
346	4.193	21.56	380.032	1566		0	62.63	380.0325	1
347	2.112	18.34	232.0599	1561		0	59.62	232.0605	1
348	14.565	14.44	191.9451	1552		0	66.63	191.9456	1
349	9.295	15.77	230.9566	1524		0	59.52	230.9571	1
350	13.53	20.96	452.92	1523		0	56.84	452.9206	1
351	2.276	14.9	161.0465	1519		0	55.84	161.0471	1
352	3.393	20.43	357.9836	1516		0	57.23	357.9841	1
353	13.392	17.72	242.942	1508		0	56.59	242.9426	1
354	6.742	28.46	597.1542	1505		0	60.19	597.1547	1
355	6.101	23.45	443.0246	1503		0	54.42	443.0252	1
356	14.999	15.13	218.9308	1500		0	70.96	218.9313	1
357	12.365	22.24	327.2174	1490		0	53.32	327.218	1
358	9.861	15.84	230.9553	1481		0	63.21	230.9559	1
359	4.105	19.93	477.0184	1476		0	53.82	477.0189	1
360	2.143	14.32	180.9733	1449		0	57.83	180.9739	1
361	13.953	17.76	310.9285	1444		0	78.12	310.9291	1
362	4.905	23.41	373.1102	1439		0	59.51	373.1107	1
363	7.537	14.32	180.9724	1426		0	52.49	180.9729	1
364	3.113	21.05	286.1766	1403		0	65.67	286.1772	1
365	5.962	26.64	491.1165	1395		0	51.36	491.117	1

366	11.83	18.45	229.1432	1395		0	52.04	229.1437	1
367	11.343	18.36	273.9918	1392		0	67.5	273.9923	1
368	15.133	20.94	446.9042	1374		0	50.12	446.9048	1
369	3.721	17.02	173.0089	1357	140.5	1	59.51	174.0162	1
370	4.167	26.1	623.0858	1350	206.3	1	54.28	624.093	1
371	4.117	17.2	211.0612	1349		0	55.42	211.0618	1
372	4.022	14.34	180.9727	1347		0	62.82	180.9732	1
373	4.006	15.29	153.055	1344		0	76.3	153.0556	1
374	11.835	14.08	130.9669	1332		0	50.26	130.9674	1
375	10.546	19.76	271.0605	1323		0	51.36	271.061	1
376	13.976	17.8	310.9281	1308		0	54.84	310.9286	1
377	10.656	17.68	242.9425	1288		0	50.5	242.943	1
378	11.437	15.79	190.0179	1280		0	64.13	190.0185	1
379	13.694	15.17	216.9336	1271		0	74.91	216.9341	1
380	5.349	20	317.0294	1234		0	62.35	317.0299	1
381	3.221	14.39	180.9738	1207		0	54.48	180.9743	1
382	2.835	14.8	169.0143	1200		0	50.32	169.0148	1
383	6.219	21.18	332.1225	1194		0	62.56	332.1231	1
384	2.57	18.98	287.0334	1164		0	50.82	287.034	1
385	7.375	19.05	300.9985	1157		0	51.96	300.999	1
386	4.9	21.8	356.1433	1154		0	64.35	356.1439	1
387	11.158	19.67	319.976	1140		0	58.9	319.9766	1
388	6.384	23.7	584.6241	1129		0	55.2	584.6247	1
389	4.44	19.21	260.0368	1127		0	66.21	260.0374	1
390	4.549	23.43	485.0584	1099		0	62.94	485.0589	1
391	4.424	22.45	440.9911	1098		0	50.46	440.9916	1
392	4.806	23.38	358.1962	1095		0	55.64	358.1968	1
393	5.311	19.19	290.0736	1092		0	56.54	290.0742	1
394	6.113	19.6	293.0895	1080		0	64.77	293.09	1
395	6.547	26.97	492.119	1071	214.5	1	60.83	493.1262	2
396	7.5	14.34	180.9733	1066		0	51.86	180.9739	1
397	6.404	19.23	287.0148	1040		0	65.4	287.0153	1
398	11.385	22.62	378.1487	1008		0	52.05	378.1492	1
399	8.497	23.94	436.1321	997		0	57.26	436.1326	1
400	12.435	15.78	189.0166	995		0	61.25	189.0172	1
401	2.973	19.01	292.0078	982		0	57.84	292.0084	1
402	15.258	17.43	316.829	959	139.3	1	57.66	317.8363	2
403	4.548	14.67	131.0722	952		0	57.88	131.0727	1
404	5.98	22.37	420.031	951		0	50.66	420.0315	1
405	4.45	20.04	306.0232	946		0	54.79	306.0237	1
406	4.169	17.35	344.0142	945	138.2	1	68.87	345.0215	1
407	4.52	19.56	265.0289	931	158.1	1	56.3	266.0362	1
408	9.096	24.75	473.0797	921		0	53.12	473.0802	1
409	6.812	19.5	378.9171	897		0	54.84	378.9177	1
410	13.464	17.71	310.9293	895		0	53.05	310.9298	1
411	4.957	29.51	577.1316	869	234.2	1	52.2	578.1388	1
412	3.237	22.24	413.062	865		0	55.24	413.0626	1
413	4.288	23.54	707.2207	829		0	53.85	707.2212	1
414	4.582	17.81	243.0464	789		0	54.5	243.047	1
415	4.988	20.07	331.0047	785		0	53.05	331.0052	1
416	3.417	14.32	180.9728	782		0	51.7	180.9734	1
417	15.562	21.89	311.1652	772		0	52.1	311.1658	1
418	15.148	15.24	220.9277	768		0	56.84	220.9282	1

419	13.35	17.81	310.9284	755	0	50.74	310.929	1
420	13.867	11.81	178.8437	755	0	56.64	178.8442	1
421	9.344	13.57	152.9782	745	0	52.28	152.9788	1
422	3.406	20.55	317.0872	729	0	52.98	317.0878	1
423	4.19	16.12	238.9805	718	0	51.89	238.981	1
424	4.145	22.32	312.0446	699	0	53.41	312.0452	1
425	15.684	23.29	311.1664	697	0	51.24	311.167	1
426	12.121	15.76	189.015	678	0	50.49	189.0156	1
427	6.947	24.46	465.1044	572	0	51.01	465.105	1

D.3.2. LC-TOF

ID	RT	Mass	Abund	Score
1	11.193	190.0244	31512360	100
2	5.183	290.079	9486124	100
3	4.169	312.0484	8579934	100
4	6.002	290.079	7318316	100
5	11.192	402.0299	6192959	100
6	4.55	176.0687	6135209	100
7	6.405	198.053	4988157	100
8	4.953	578.1423	3147660	100
9	5.808	578.1426	2606421	100
10	5.005	296.053	1554592	100
11	5.44	180.0425	1510432	100
12	4.42	130.0263	1280638	100
13	4.55	374.1185	1005234	100
14	6.1	292.0948	1003295	100
15	11.227	258.0119	984035	87
16	4.024	316.116	933156	100
17	5.184	358.0665	916510	100
18	6.002	358.0665	861822	100
19	11.191	614.0361	830949	100
20	4.169	646.0785	795620	100
21	6.336	367.1266	788276	100
22	7.411	478.0747	785398	100
23	11.193	470.0173	769868	100
24	5.067	578.1424	762216	100
25	9.687	302.0428	687947	100
26	9.753	208.0737	685291	100
27	4.42	176.0687	670577	100
28	4.173	380.0356	629776	100
29	4.433	154.0268	607872	100
30	7.514	626.1848	587320	100
31	11.156	258.0117	579538	85.3
32	2.961	144.0425	568069	100
33	5.5	326.1002	549852	100
34	2.961	162.0531	549821	100
35	4.315	617.1164	534206	100
36	5.691	448.1582	531921	100
37	2.96	230.0403	515033	100
38	8.403	318.0376	507204	100
39	6.469	866.2057	504359	100
40	11.191	608.0189	504246	100
41	8.202	390.1315	499277	100
42	3.438	154.0634	498495	100
43	6.316	166.0633	481088	100
44	11.394	243.1837	463897	100
45	3.183	230.0404	440765	100
46	4.171	300.0336	432589	100
47	6.817	510.137	420758	100
48	4.102	220.0586	414960	100
49	5.807	646.1301	414676	100
50	4.419	244.0562	413527	100
51	3.682	306.0742	408854	100
52	4.819	296.0533	408355	100
53	5.004	444.1996	407605	100
54	3.35	430.1685	405481	100
55	3.814	594.1372	403400	100
56	5.319	132.0788	397796	100
57	4.556	244.0562	382035	100
58	5.526	326.0637	381458	100
59	5.816	326.1002	379861	100
60	5.512	866.2061	375558	100
61	11.192	464.0001	371207	100
62	3.745	866.2057	366423	100
63	3.167	157.0741	351344	100
64	11.192	275.0017	349646	100
65	4.167	334.0299	349385	86.7
66	6.512	164.0472	340881	100
67	14.853	195.0898	334973	100
68	4.954	646.1299	332277	100
69	3.523	386.1425	326698	100
70	7.41	782.2057	316820	100
71	3.709	220.0584	309888	100
72	6.239	428.041	309152	87
73	4.42	374.1188	306935	100
74	7.157	436.137	306070	100
75	6.002	336.0845	290527	100
76	7.412	626.1845	285757	100
77	8.12	508.1216	285436	100
78	7.527	450.116	282449	100
79	5.183	404.0715	282071	100
80	8.082	782.2062	269593	100
81	4.553	1097.0702	266676	100
82	9.804	228.0788	263003	100
83	4.17	180.0426	260629	100
84	3.584	369.1059	255571	100
85	6.014	154.0266	255498	100
86	11.192	676.0063	254441	100
87	11.245	325.9989	252398	100
88	5.006	364.0405	244982	100
89	13.459	294.1832	238503	100
90	6.655	730.1536	238033	100
91	2.959	346.0872	236543	100
92	8.091	188.1051	236112	100
93	11.191	820.0247	236034	100

94	2.293	162.0533	235623	100
95	5.964	432.1993	234943	95.4
96	8.112	182.0581	234302	100
97	4.928	294.1314	232968	100
98	5.606	866.2059	231215	92.8
99	7.054	205.074	227249	100
100	2.962	118.0631	227020	100
101	3.845	488.0734	225551	100
102	4.025	384.1029	222263	100
103	6.579	578.1419	221194	100
104	3.288	400.1579	220723	100
105	11.194	146.0345	220423	100
106	7.703	354.1312	214193	100
107	5.185	426.0534	212637	100
108	6.781	480.0902	208476	100
109	4.212	182.058	207263	99.9
110	7.412	500.0563	205757	100
111	6.001	404.0714	204849	100
112	4.657	594.1373	203843	100
113	5.125	686.1304	201212	100
114	3.18	346.0873	200908	100
115	6.338	435.1138	200337	100
116	3.434	316.0792	200014	100
117	11.702	232.1099	196721	100
118	4.553	396.1005	194130	100
119	3.524	280.1162	192119	100
120	5.752	432.1991	191981	100
121	5.183	336.0842	191006	100
122	5.183	326.0556	190689	100
123	4.315	639.0981	188844	100
124	5.183	420.0368	187285	100
125	11.192	682.0231	185205	100
126	4.551	572.169	180736	100
127	6.002	426.0536	180553	100
128	8.626	500.1465	180398	100
129	7.258	168.042	179807	100
130	5.02	166.0269	179727	100
131	3.072	154.0268	178643	100
132	6.101	360.082	170336	100
133	6.002	326.0557	169917	100
134	6.146	398.0307	169461	86.7
135	6.002	420.0367	168047	100
136	6.406	266.0402	166761	100
137	6.791	508.1211	164752	100
138	4.974	306.0741	163496	100
139	6.941	398.0667	163209	100
140	5.384	686.1302	161520	100
141	5.856	866.2061	160804	100
142	11.236	319.982	158182	100
143	11.377	330.2404	156910	100
144	4.239	176.0686	156585	100
145	11.15	325.9989	156416	100
146	4.135	594.1371	154357	100
147	4.427	352.0769	154289	100
148	4.193	402.0171	152237	87
149	6.044	428.1889	152077	100
150	2.959	298.0274	149012	100
151	5.691	516.1452	148334	100
152	5.42	398.0666	147790	100
153	5.183	648.1452	146748	100
154	4.159	383.1074	146306	100
155	7.429	596.1736	145829	100
156	6.069	686.1302	145607	100
157	3.352	498.1559	145483	100
158	7.709	340.0791	144775	100
159	6.181	190.0845	142557	100
160	7.767	364.0792	142023	100
161	3.407	207.0534	141599	100
162	7.475	510.2309	140623	100
163	3.864	174.0529	140522	99.8
164	8.203	458.1186	138205	100
165	5.248	326.1	137491	98.8
166	5.454	448.1577	136403	100
167	7.399	578.142	136268	100
168	5.259	414.0255	135873	89.7
169	5.319	200.0663	135794	100
170	10.763	328.2246	134182	99
171	5.875	242.1268	133859	100
172	11.191	826.0416	132565	96.8
173	4.193	184.0375	132388	100
174	5.183	353.0743	131596	100
175	6.1	338.1004	128626	100
176	4.13	112.0164	127986	100
177	6.314	234.0504	127800	100
178	11.19	418.0037	126958	100
179	5.197	422.1572	126493	100
180	4.174	310.032	126079	100
181	5.345	230.1057	125891	100
182	7.269	302.0057	125336	100
183	5.276	510.1371	124074	100
184	11.193	247.983	123491	100
185	5.844	686.1307	123100	100
186	5.719	398.0669	122059	100
187	3.693	244.0584	121850	100
188	3.18	162.0533	121698	100
189	6.636	466.111	120465	100

190	8.082	452.1105	119947	100	238	8.237	640.1997	94587	95.9
191	3.716	358.0868	119214	100	239	11.113	316.058	93502	100
192	3.156	220.0586	118449	100	240	7.514	648.1666	92941	100
193	5.501	394.0875	118275	100	241	6.404	312.0457	92692	100
194	4.095	244.0562	117861	100	242	4.162	695.1557	92335	100
195	8.549	434.1213	116047	100	243	3.182	482.1059	92260	100
196	5.739	296.1468	115591	100	244	11.191	888.0115	91043	100
197	3.584	592.1095	115480	100	245	3.584	437.0928	91031	100
198	6.097	882.2006	115214	100	246	11.255	393.986	90776	100
199	4.11	288.0458	113656	100	247	11.25	387.969	90589	100
200	6.732	174.0892	113217	100	248	11.224	538.0047	90036	87
201	4.941	882.2001	112617	100	249	5.469	244.1789	89794	100
202	6.003	353.0744	112235	100	250	9.263	264.136	89670	100
203	6.008	444.1053	108904	100	251	8.081	850.1929	89204	100
204	11.394	311.1708	108220	100	252	4.938	214.0456	88122	98.1
205	6.001	648.1455	107394	100	253	4.14	554.0882	87323	100
206	5.215	132.0788	106118	100	254	4.314	661.0797	87219	100
207	4.026	430.1082	105804	100	255	5.182	488.0237	86789	100
208	5.3	398.067	105609	100	256	4.436	702.1121	86413	100
209	5.808	668.1123	104133	100	257	5.304	316.1156	86174	100
210	4.421	306.0266	103555	100	258	6.733	494.0694	86068	100
211	5.061	646.13	103345	99.2	259	6.78	586.2256	85750	100
212	7.489	494.1056	103190	100	260	5.44	248.0297	85671	100
213	5.004	512.1867	102942	100	261	2.96	302.0977	85590	100
214	5.625	488.1524	102121	100	262	6.42	1070.2684	84769	100
215	3.656	162.0894	101742	100	263	6.003	782.2055	84644	100
216	6.818	578.125	100092	100	264	7.41	850.1931	84063	100
217	6.755	560.1161	100025	100	265	5.354	426.173	83858	95.7
218	4.351	230.1633	99946	100	266	13.848	379.293	83758	100
219	8.204	436.1363	99937	100	267	6.375	866.2055	83606	100
220	4.804	414.1735	99729	100	268	6.032	488.1525	83551	100
221	3.737	312.0481	99689	100	269	4.172	690.0424	82876	100
222	5.86	512.1525	99534	100	270	8.091	210.0871	82805	100
223	4.096	176.0687	99432	100	271	9.685	370.0297	82708	100
224	3.184	292.0109	99215	81.9	272	4.55	566.1521	82519	100
225	4.173	463.9877	98786	98.6	273	5.817	394.0874	82155	100
226	4.775	244.0562	98784	100	274	5.527	394.0509	81696	100
227	5.332	158.0579	98711	100	275	4.442	222.0143	81632	100
228	9.468	546.1885	98432	100	276	5.115	594.1371	81445	100
229	5.951	320.0533	98147	100	277	5.391	452.1315	81284	100
230	5.009	386.022	97978	100	278	4.527	266.0383	81246	87
231	11.152	319.9818	97808	100	279	3.682	374.0611	80936	100
232	5.062	182.058	97777	100	280	7.156	504.124	80886	100
233	3.846	510.055	97662	100	281	4.024	452.0899	80152	100
234	11.26	192.0789	97287	100	282	3.181	414.0747	79610	100
235	6.096	450.1161	96329	100	283	6.704	348.1238	78370	100
236	6.096	488.1527	95667	100	284	6.556	276.1112	78231	100
237	4.82	364.0403	94714	100	285	6.488	462.173	77911	100

286	7.513	694.1719	77905	100
287	4.951	614.1183	77770	100
288	6	488.024	77733	100
289	3.712	288.0454	77345	100
290	2.966	186.0504	77330	100
291	6.101	314.0765	77246	100
292	4.553	412.0665	77183	100
293	11.193	479.9727	77095	100
294	5.061	294.1316	76695	100
295	3.181	359.998	76502	96.8
296	6.001	892.2187	76375	100
297	4.17	662.0452	76360	100
298	7.648	170.0215	76274	100
299	10.48	906.2669	75877	100
300	7.527	518.1031	75705	100

Bibliography

[1] Abu B. Kanu et al. “Ion mobility–mass spectrometry.” In: *Journal of Mass Spectrometry* 43.1 (Jan. 1, 2008), pp. 1–22. DOI: 10.1002/jms.1383 (cit. on pp. 1, 6).

[2] Riccardo Flamini. “Mass spectrometry in grape and wine chemistry. Part I: Polyphenols.” In: *Mass Spectrometry Reviews* 22.4 (July 1, 2003), pp. 218–250. DOI: 10.1002/mas.10052 (cit. on p. 1).

[3] Darko Modun et al. “The increase in human plasma antioxidant capacity after red wine consumption is due to both plasma urate and wine polyphenols.” In: *Atherosclerosis* 197.1 (Mar. 2008), pp. 250–256. DOI: 10.1016/j.atherosclerosis.2007.04.002 (cit. on p. 1).

[4] Stéphane Quideau et al. “Plant Polyphenols: Chemical Properties, Biological Activities, and Synthesis.” In: *Angewandte Chemie International Edition* 50.3 (Jan. 17, 2011), pp. 586–621. DOI: 10.1002/anie.201000044 (cit. on p. 1).

[5] Øyvind M. [Hrsg Andersen and Jonathan E. Brown. *Flavonoids : chemistry, biochemistry and applications*. Boca Raton, Flaua: CRC Press, 2006. 1237 pp. (cit. on p. 3).

[6] Kelly E Heim, Anthony R Tagliaferro, and Dennis J Bobilya. “Flavonoid antioxidants: chemistry, metabolism and structure-activity relationships.” In: *The Journal of Nutritional Biochemistry* 13.10 (Oct. 2002), pp. 572–584. DOI: 10.1016/S0955-2863(02)00208-5 (cit. on p. 3).

[7] Ilse Zündorf. “Teedrogen und Phytopharmaka. Von Max Wichtl (Hrsg.)” In: *Pharmazie in unserer Zeit* 38.2 (Mar. 1, 2009), pp. 192–193. DOI: 10.1002/pauz.200990017 (cit. on p. 3).

[8] Ana García-Lafuente et al. “Flavonoids as anti-inflammatory agents: implications in cancer and cardiovascular disease.” In: *Inflammation Research* 58.9 (Apr. 21, 2009), pp. 537–552. DOI: 10.1007/s00011-009-0037-3 (cit. on p. 3).

[9] Di Zhang et al. “Analysis of the antioxidant capacities of flavonoids under different spectrophotometric assays using cyclic voltammetry and density functional theory.” In: *Journal of Agricultural and Food Chemistry* 59.18 (Sept. 28, 2011), pp. 10277–10285. DOI: 10.1021/jf201773q (cit. on p. 4).

[10] Priyanka Chatterjee et al. “Evaluation of anti-inflammatory effects of green tea and black tea: A comparative in vitro study.” In: *Journal of Advanced Pharmaceutical Technology & Research* 3.2 (2012), pp. 136–138. DOI: 10.4103/2231-4040.97298 (cit. on p. 4).

[11] Patricia Diaz et al. "Antioxidant and anti-inflammatory activities of selected medicinal plants and fungi containing phenolic and flavonoid compounds." In: *Chinese Medicine* 7.1 (2012), p. 26. DOI: 10.1186/1749-8546-7-26 (cit. on p. 4).

[12] Dragan Amic et al. "SAR and QSAR of the Antioxidant Activity of Flavonoids." In: *Current Medicinal Chemistry* 14.7 (Mar. 1, 2007), pp. 827–845. DOI: 10.2174/092986707780090954 (cit. on p. 4).

[13] Ju-Mi Jeong et al. "Antioxidant and Chemosensitizing Effects of Flavonoids with Hydroxy and/or Methoxy Groups and Structure-Activity Relationship." In: *Journal of Pharmacy & Pharmaceutical Sciences* 10.4 (Oct. 26, 2007), pp. 537–546 (cit. on p. 4).

[14] S.K. Gunda, S.K.M. Narasimha, and M. Shaik. "P56lck kinase inhibitor studies: A 3D QSAR approach towards designing new drugs from flavonoid derivatives." In: *International Journal of Computational Biology and Drug Design* 7.2 (2014), pp. 278–294. DOI: 10.1504/IJCBDD.2014.061648 (cit. on p. 4).

[15] Leonhard Jaitz et al. "LC–MS/MS analysis of phenols for classification of red wine according to geographic origin, grape variety and vintage." In: *Food Chemistry* 122.1 (Sept. 1, 2010), pp. 366–372. DOI: 10.1016/j.foodchem.2010.02.053 (cit. on pp. 4, 13).

[16] Marcello Iriti and Sara Vitalini. "Chemical Diversity of Grape Products, a Complex Blend of Bioactive Secondary Metabolites." In: *The Natural Products Journale* 1.1 (July 1, 2011), pp. 71–74. DOI: 10.2174/2210315511101010071 (cit. on p. 4).

[17] M. E. Alañón, M. S. Pérez-Coello, and M. L. Marina. "Wine science in the metabolomics era." In: *TrAC Trends in Analytical Chemistry* 74 (Dec. 2015), pp. 1–20. DOI: 10.1016/j.trac.2015.05.006 (cit. on p. 4).

[18] Ramon Díaz et al. "Told through the wine: A liquid chromatography–mass spectrometry interplatform comparison reveals the influence of the global approach on the final annotated metabolites in non-targeted metabolomics." In: *Journal of Chromatography A* 1433 (Feb. 12, 2016), pp. 90–97. DOI: 10.1016/j.chroma.2016.01.010 (cit. on p. 4).

[19] Franz Bucar, Abraham Wube, and Martin Schmid. "Natural product isolation – how to get from biological material to pure compounds." In: *Natural Product Reports* 30.4 (Mar. 12, 2013), pp. 525–545. DOI: 10.1039/C3NP20106F (cit. on p. 5).

[20] Bénédicte Lorrain et al. "Evolution of Analysis of Polyhenols from Grapes, Wines, and Extracts." In: *Molecules* 18.1 (Jan. 16, 2013), pp. 1076–1100. DOI: 10.3390/molecules18011076 (cit. on p. 5).

[21] Ghada H. Yassin et al. "Investigation of isomeric flavanol structures in black tea thearubigins using ultraperformance liquid chromatography coupled to hybrid quadrupole/ion mobility/time of flight mass spectrometry." In: *Journal of Mass Spectrometry* 49.11 (Nov. 1, 2014), pp. 1086–1095. DOI: 10.1002/jms.3406 (cit. on p. 6).

[22] H. E. Revercomb and E. A. Mason. "Theory of plasma chromatography/gaseous electrophoresis. Review." In: *Analytical Chemistry* 47.7 (June 1, 1975), pp. 970–983. DOI: 10.1021/ac60357a043 (cit. on pp. 6, 7).

[23] Iain Campuzano et al. "Structural Characterization of Drug-like Compounds by Ion Mobility Mass Spectrometry: Comparison of Theoretical and Experimentally Derived Nitrogen Collision Cross Sections." In: *Analytical Chemistry* 84.2 (Jan. 17, 2012), pp. 1026–1033. DOI: 10.1021/ac202625t (cit. on p. 6).

[24] Matthew F. Bush, Iain D. G. Campuzano, and Carol V. Robinson. "Ion Mobility Mass Spectrometry of Peptide Ions: Effects of Drift Gas and Calibration Strategies." In: *Analytical Chemistry* 84.16 (Aug. 21, 2012), pp. 7124–7130. DOI: 10.1021/ac3014498 (cit. on p. 6).

[25] Jody C. May and John A. McLean. "Ion Mobility-Mass Spectrometry: Time-Dispersive Instrumentation." In: *Analytical Chemistry* 87.3 (Feb. 3, 2015), pp. 1422–1436. DOI: 10.1021/ac504720m (cit. on p. 6).

[26] Larissa S. Fenn et al. "Characterizing ion mobility-mass spectrometry conformation space for the analysis of complex biological samples." In: *Analytical and Bioanalytical Chemistry* 394.1 (Feb. 27, 2009), pp. 235–244. DOI: 10.1007/s00216-009-2666-3 (cit. on p. 9).

[27] *6200 Series Accurate-Mass Time-of-Flight (TOF) LC/MS — Agilent*. URL: http://www.chem.agilent.com/en-US/products-services/Instruments-Systems/Mass-Spectrometry/6200-Series-Accurate-Mass-Time-of-Flight-(TOF)-LC-MS/Pages/default.aspx (visited on 07/08/2015) (cit. on p. 9).

[28] *6560 Ion Mobility Q-TOF LC/MS — Agilent*. URL: http://www.chem.agilent.com/en-US/products-services/Instruments-Systems/Mass-Spectrometry/6560-Ion-Mobility-Q-TOF-LC-MS/Pages/default.aspx (visited on 07/08/2015) (cit. on pp. 9, 10).

[29] Souji Rokushika et al. "Resolution measurement for ion mobility spectrometry." In: *Analytical Chemistry* 57.9 (Aug. 1, 1985), pp. 1902–1907. DOI: 10.1021/ac00286a023 (cit. on pp. 11, 12).

[30] Prabha Dwivedi, Albert J. Schultz, and Herbert H. Hill. "Metabolic Profiling of Human Blood by High Resolution Ion Mobility Mass Spectrometry (IM-MS)." In: *International journal of mass spectrometry* 298.1 (Dec. 2010), pp. 78–90. DOI: 10.1016/j.ijms.2010.02.007 (cit. on p. 12).

[31] Brian H. Clowers et al. "Enhanced Ion Utilization Efficiency Using an Electrodynamic Ion Funnel Trap as an Injection Mechanism for Ion Mobility Spectrometry." In: *Analytical chemistry* 80.3 (Feb. 1, 2008), pp. 612–623. DOI: 10.1021/ac701648p (cit. on p. 15).

[32] B. Magnusson and U. Örnemark (eds.) *Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics*. 2014 (cit. on p. 17).

Marian Došen

Persönliche Daten

Geburtsort und Datum:	Salzburg, Österreich | 14 März 1986
Adresse:	Fasangasse 41/2/2, 1030, Wien, Österreich
Telefon:	+43 650 2424190
Email:	marislav@gmx.at

Arbeitserfahrung

Aktuell
Feb 2016

Midex Bau- und Handels -GmbH
Netzwerkadministration
Installation eines kleinen Firmennetzwerks und Abwicklung der Datensicherung, Implementierung einer Domain und Bereitstellung der Webpräsenz.

2012-2013

Lehrkraft beim Lernquadrat, Wien
Chemie und Mathematik
Unterricht und Bürotätigkeiten, sowie Kundenkontakt und Organisation

2011-2012

Sprechstundenhilfe Univ.-Doz. Dr. Margot Schmitz, *Fachärztin für Neurologie und Psychiatrie*
Erfahrungen mit dem Gesundheitswesen, neurologischen Erkrankungen und deren pharmakologischer Therapie, sowie Organisation und Koordination.

2006-2016

Nachhilfetätigkeiten Chemie und Mathematik
Hauptsächlich Schüler der HTL Rosensteingasse

Ausbildung

Februar 2016	Diplomstudium Magister Pharmaciae, **Universität Wien**, Wien
October 2006	Matura an der HTL Rosensteingasse für chemische Industrie Abteilung für Leder und Naturstofftechnologie

Sprachen

Deutsch:	Muttersprache
Bosnisch, Kroatisch, Serbisch:	Vatersprache
Englisch:	akzeptabel

Computer Skills

Basiswissen:	html, Linux, ubuntu, LaTeX, Netzwerktechnik
Fortgeschritten:	Excel, Word, PowerPoint, Windowsplattformen generell

Interessen und Aktivitäten

Chemie, Medizinalpflanzen
Sportklettern, Reisen

Marian Došen

Personal Data

Place and Date of Birth:	Austria | 14 March 1986
Address:	Fasangasse 41/2/2, Vienna, Austria
Phone:	+43 650 2424190
email:	marislav@gmx.at

Work Experience

Current
Feb 2016 | Network-administration at Midex Bau- und HandelsgmbH, Vienna
Setting up domain, network and data security for a small company.

2012 - 2013 | Teaching at Lernquadrat, Vienna
Mathematics and Chemistry

2011 - 2012 | Assistant at Univ.-Doz. Dr. Margot Schmitz, Vienna
Organization and Coordination.

2006 - 2016 | Teaching to Students, Vienna
Learning Mathematics and Chemistry with students from my former school.

Education

Feb 2016 Diploma in Pharmacy, **University of Vienna**, Vienna

Oct 2006 High school degree in Industrial Chemistry (http://hblva17.ac.at/)

Languages

English:	Fluent
German:	Mother-tongue
Bosnian-Croatian-Serbian:	Proficient

Computer Skills

Basic Knowledge:	html, Linux, ubuntu, Network-administration LaTeX
Intermediate Knowledge:	vba, Excel, Word, PowerPoint

Interests and Activities

Medicinal plants, Sports-climbing