Conversion of Refractometric Dry Substance
Into Real Dry Substance for Quentin Molasses*

G. Sgualdino, G. Vaccari and G. Mantovani

INTRODUCTION

The determination of the dry substance of impure sugar syrups by means of refractometry is normally adopted for its simplicity and performance rapidity, although it is affected by some errors.

The higher the content of the nonsugar substances in the solution examined, the more the refractometric dry substance differs from the real one, and these deviations are also related to the type of such impurities whether they are ions or molecules.

It is clear that, among all the factory juices, the ones which show the highest deviation between refractometric and real dry substance are the molasses which have the most unfavorable sucrose/nonsucrose ratio.

In the case of traditional beet molasses it is known that the refractometric dry substance, determined by the 1:1 dilution method, is always higher than the dry substance, which we can consider as the real one, determined by the Karl-Fischer method. This difference is in general around 1.5 units and therefore this value could be used to correct, although approximately, the refractometric dry substance to obtain the real one.

On the contrary, for Quentin molasses, as pointed out in a previous paper (1), the differences are very variable and also can be remarkably high exceeding the five units for molasses obtained from juices coming from a very hard Na^+-K^+/Mg^{++} exchange. A good correlation was found (1) among the values of the difference between the refractometric and real dry substances and the contents of magnesium ions of various Quentin molasses obtained by means of different exchange levels.

    With the aim of pointing out as far as possible the
correction to be used, which seems to be ascribed to the
higher hydration capacity of the magnesium ions in com-
parison to the alkaline ones, and to the potassium ions in
particular (2), we carried out a series of tests on the
effect of magnesium and potassium ion additions, as
chlorides, on the dry substance refractometric determina-
tion. These tests were performed, not only to confirm the
correlation pointed out in the previous paper (1), but
also to be able to propose, from a general point of view,
the type of correction which is to be made on refracto-
metric dry substance of Quentin molasses to obtain the
real one and in the meantime to calculate their exhaustion
level with higher precision.

    Also during the last session of ICUMSA in Dublin (3),
the Referee of Subject No. 13 recommended further study of
the corrections required to convert refractometer solids
to true solids.

MATERIALS AND METHODS

    Two types of molasses of different origin and obtained
through a process without Quentin exchange were studied.
These molasses, having the composition shown in Table 1,
were added with increasing amounts of KCl and $MgCl_2 \cdot 6H_2O$,
respectively, with the aim of changing their potassium and
magnesium ion contents. The addition of salts was per-
formed as follows: about 600-700 grams of molasses were
put into a flask stirred by an airtight device. After in-
troduction of the desired amount of salt the flask was put
into a thermostatic bath at 60°C overnight and the mixture
was stirred constantly. In this manner the salt was com-
pletely dissolved in the molasses sample which after
cooling, was again analyzed determining Brix (dil. 1:1)
and the water content, by the Karl-Fischer method we de-
scribed in detail in a previous paper (4). The choice of
the amount of molasses to which the various amounts of
salt were to be added was made taking into account the
need to minimize the error during the weighing of the mag-
nesium chloride which is highly hygroscopic. This salt

was, however, constantly preserved in a dessicator and
periodically controlled by Karl-Fischer titration to be
sure that the water content corresponded exactly to only
the six molecules of crystallization water per magnesium
chloride molecule.

Table 1. Analytical data of the two molasses used in the tests.

Analytical data	Molasses 1	Molasses 2
Refractometric dry substance%	82.2	82.6
Dry subsance by Karl-Fischer method %	80.66	80.98
Polarization	49.36	47.66
Reducing sugars %	0.07	0.22
pH	8.76	8.73
Sodium (meq.%grams molasses)	79.6	77.4
Potassium " "	101.8	88.2
Calcium " "	11.3	5.5
Magnesium " "	1.2	0.4

The percentages of the two salts were added in the
range between 2 and 10% molasses, always on the basis of
the anhydrous salt. This range was chosen bearing in mind
the possible composition variation of the two ions, (in-
crease for the magnesium ion and decrease for the potas-
sium ion), which can be set up for molasses obtained
through a Quentin process in comparison to molasses ob-
tained through a traditional process. In this way it is
possible to directly transpose the data which can be ob-
tained from the tests to the real Quentin molasses without
using any extrapolation.

RESULTS AND DISCUSSION

The determination of the dry substance of molasses in
the presence of the two cited salts by means of the Karl-
Fischer method allowed us to confirm the reliability of
this type of analysis for the determination of the real

dry substance.   In fact,   after each addition of salt the
amount   of   water we determined was exactly equal   to   the
calculated one,   also in the case of the addition of $MgCl_2$
$\cdot 6H_2O$.   By calculating,   for each salt addition, the dif-
ferences   between   the real dry substance content and   the
refractometric   reading   it was possible to draw   the   two
lines shown in Figure 1.   The increase of the error which
is   made on the refractometric dry substance with the   in-
crease   of the amount of magnesium added is clearly   seen,
and moreover,   though,   much less notable, the addition of
potassium causes a decrease of the error on the   refracto-
metric measurement.   Therefore we can assume that the re-
placement   of   potassium by magnesium through the   Quentin
exchange   involves   an analytical error in   the   refracto-
metric dry substance determination which results from   the
contribution of two factors.   One factor is due to the in-
troduction   of   the magnesium ion which increases the   re-
fractometric dry substance in comparison to the real   one.
The   other   factor   can be identified as   the   removal   of
potassium   ions whose presence seems to   decrease,   though
not   much,   the difference between refractometric and real
dry substances.   Bearing in mind the comparatively   small
contribution of the latter factor, and moreover that it is
impossible   to   know from a Quentin molasses analysis   the
amount of potassium which was removed, because an increase
in   the magnesium content does not correspond to an   equal
decrease in the potassium content,   we can devote our   at-
tention   to the magnesium alone.   The regression analysis
carried out on the data we have collected allows us to ob-
tain the following equation:

$y = 0.01643\,x + 1.6387$ $r = 0.992$

where   y is the difference between the refractometric   dry
substance   and the result determined by   the   Karl-Fischer
method,   whereas   x is the magnesium content expressed   in
milliequivalents   %   refractometric dry   substance.   From
such an equation,   on the basis of the molasses   magnesium
content   we can obtain the value that is to be substracted
from   the refractometric dry substance to obtain the   real

one. If we eliminate the constant term from this equation
we obtain a relation which allows us to calculate the
value to be subtracted from the Brix we have measured to
obtain the Brix of a hypothetical molasses which we would
have obtained in the absence of Quentin exchange.   In
fact, the magnesium content of the traditional molasses is
in general so low that it cannot affect the refractometric
measurement error and the influence of potassium is rela-
tively small.   This is only reasonably valid supposing
that the exchange does not notably alter the other com-
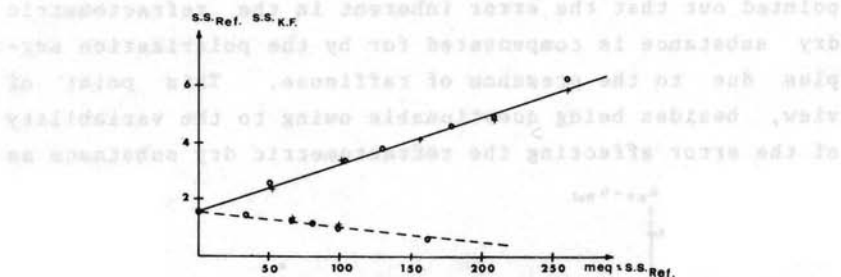ponents of the solution apart from the cation exchange.

Figure 1.   Differences between the content of refractometric
            and real (K. F.) dry substances in relation to the
            salt added.
            _____ Magnesium Chloride   ° Molasses 1
            - - - - - Potassium Chloride   x Molasses 2

In our tests we have not taken into consideration the
sodium ion.   In fact, this ion, which, although less pre-
ferred in comparison to potassium, can be replaced by mag-
nesium ions during the Quentin process, does not show, in
general, a decrease of its content compared with molasses
resulting from traditional processing.   In fact, although
a portion of this ion is eliminated by the ion exchange
resins, it is in general more or less replaced by the so-
dium hydrate additions normally carried out to maintain
the pH of the juices at the optimum values.
     We have to point out here that the method we adopted
of adding the two cations in the form of chlorides could
be affected by an error due to the eventual interference
of the chloride ion with the refractometric measurement.

However this influence, as it is known, is very low (5)
owing to the relatively low charge density of the chloride
ion, so that we judge that it can be ignored. On the
other hand, the equation obtained after addition of magne-
sium chloride to traditional molasses compares well to the
one obtained by analyzing a high number of Quentin molas-
ses of different origin (1), and this fact confirms the
validity of the type of correction we propose.

As far as the effect of the inaccuracy of the refrac-
tometric dry substance on the Quentin molasses purities e-
valuation is concerned, Oldfield and Coworkers (6) have
pointed out that the error inherent in the refractometric
dry substance is compensated for by the polarization sur-
plus due to the presence of raffinose. This point of
view, besides being questionable owing to the variability
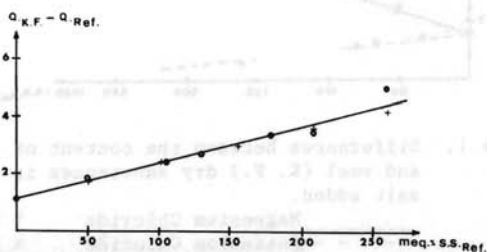of the error affecting the refractometric dry substance as

Figure 2.   Differences between real (K. F.) and refracto-
             metric purity in relation to magnesium chloride
             added.
             ° Molasses 1   x Molasses 2

a function of the different level of the ion exchange,
cannot be applied to Italian molasses where the raffinose
content is very low. It follows that as the magnesium
content increases, the purity determined refracto-
metrically on Quentin molasses decreases in comparison to
the real purity. Therefore, also for the purity we can
calculate, from the collected data, an equation which
allows us to easily correct by analytical or graphic
methods refractometric purity data to obtain the real
ones. Such equation, shown in Figure 2, is as follows:

$y = 0.0123 \, x + 1.1363$ $r = 0.977$

where y is the difference between the real (Karl-Fischer) and the refractometric purities, whereas x is the magnesium content expressed as milliequivalents % refractometric dry substance.

In conclusion we can point out that by the use of simple graphic or analytical corrections it is possible to obtain real values of dry substances and purities of Quentin molasses on the basis of their magnesium contents.

SUMMARY

On the grounds of experiments carried out on molasses in the pressence of various amounts of KCl and $MgCl_2 \cdot 6H_2O$ two equations were obtained which allow real values of dry substance and purity of Quentin molasses depending on their magnesium content, to be obtained.

ACKNOWLEDGMENTS

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