Chapter 8 A Comparison of Thermoelectric Devices Evaluation Results Obtained with a Harman Method Based and a Porcupine Method Based *zT* Meters

A. De Marchi, V. Giaretto, S. Caron, A. Tona, and A. Muscio

Abstract This paper compares the results obtained for the series resistance *R* and the dimensionless figure of merit *zT* of a variety of different thermoelectric devices with two instruments based on alternative approaches: a commercial *zT* meter (DX 3065) manufactured by RMT and based on the Harman method, and a proto-type realized at the Politecnico di Torino and based on the porcupine method. All devices were evaluated with both instruments at three different temperatures (20, 25, and 30 °C) in a climatic chamber, and results were compared. As expected from the theoretical analysis, the porcupine method consistently returned lower *R* values than those obtained by the Harman approach. Values obtained for *zT* with the two instruments are instead much more aligned, which is unexpected if thermoelectric effects

A. De Marchi (🖂)

V. Giaretto Dipartimento Energia, Politecnico di Torino, C.so Duca degli Abruzzi, 24, 10129 Torino, Italy

Unità di Ricerca, Consorzio Nazionale Interuniversitario di Scienze fisiche della Materia (CNISM), Politecnico di Torino, C.so Duca degli Abruzzi, 24, 10129 Torino, Italy

A. Muscio

Dipartimento di Elettronica e Telecomunicazioni, Politecnico di Torino, C.so Duca degli Abruzzi, 24, 10129 Torino, Italy

Unità di Ricerca, Consorzio Nazionale Interuniversitario di Scienze fisiche della Materia (CNISM), Politecnico di Torino, C.so Duca degli Abruzzi, 24, 10129 Torino, Italy e-mail: andrea.demarchi@polito.it

S. Caron • A. Tona Dipartimento di Elettronica e Telecomunicazioni, Politecnico di Torino, C.so Duca degli Abruzzi, 24, 10129 Torino, Italy

Dipartimento di Ingegneria "Enzo Ferrari", Università di Modena e Reggio Emilia, Via Vignolese 905, 41125 Modena, Italy

are assumed to be correctly accounted for. A discussion of these results is presented, with comments on extrapolations which are introduced in both approaches in order to infer relevant quantities.

Keywords Thermoelectricity • Figure of merit • zT meter • Porcupine diagram • Harman method

Introduction

Measuring the dimensionless figure of merit zT of thermoelectric devices requires a strategy to separate the voltage observed across the sample into Seebeck and ohmic contributions. Both time domain and frequency domain approaches have been used to that aim. The former yields methods [1, 2] which historically go under the name of Harman, who was the first to propose it back in the fifties; the latter leads to the porcupine method [3], which is named after the shape of the device's impedance diagram in the complex plane.

A novel zT meter has been recently developed as a variation on the concept of the Vector Impedance Meter to implement such frequency domain approach, and preliminary results obtained with a prototype instrument based on a high resolution Digital Phase Meter and Digitally Controlled Attenuators were presented [4] to the international community.

In this paper, a comparison is carried out between results obtained with a second generation prototype of the porcupine zT meter and with a commercial time domain (Harman type) instrument [5] produced by RMT (model DX 3065). In both cases, measurements of zT and R (the ohmic series resistance) were performed on a number of thermoelectric devices in a temperature controlled chamber at 20, 25, and 30 °C in order to avoid environmental disturbances and get a good estimate of temperature coefficients of the measured quantities.

Values of *R* measured with the porcupine meter turned out to be consistently lower than the so-called AC resistance R_{AC} returned by the Harman based *zT* meter. The difference between the two is discussed below, and turns out to be greater than expected from the comparative analysis of the two methods, as it has previously been [3] spelled out and is recalled in the next section.

In partial contradiction, instead, zT values obtained from the porcupine meter were not significantly different from those returned by the commercial Harman type meter. A discussion of possible reasons for this discrepancy is also proposed below.

Comparison of the Two Methods

Both considered Time Domain and Frequency Domain methods are first quickly illustrated here as implemented in the two instruments at hand. One is based on the study of the Time Domain response to strategically designed excitation current

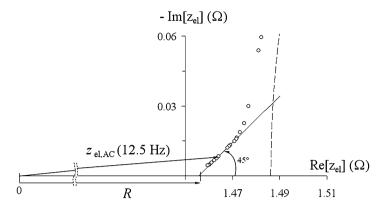


Fig. 8.1 Strategy used in the porcupine method in order to estimate the ohmic resistance *R* from electrical impedance measurements. The snout slopes at 45° at high frequencies, and *R* is taken to be its intercept on the real axis. The dashed line shows the circle that approximates the porcupine body at low frequencies. The indicated 12.5 Hz impedance point is highlighted because such is the frequency f_{AC} that was used for measurements of R_{AC} with the RMT meter

steps; the other on the study of the device's electrical impedance in the complex plane. A more complete description of both can be easily found in the open literature together with the underlying theory [3-5].

In both cases the dimensionless figure of merit zT is obtained from the ratio between resistances exhibited by the device in DC, where the developed voltage includes the Seebeck effect, and at very high frequency, where it is expected to asymptotically approach the ohmic resistance *R*. Such ratio is clearly equal to zT+1. Neither condition is experimentally viable in practice, as one is sensitive to boundary conditions and the other would in principle require operation at infinite frequency. Extrapolations are therefore necessary at both ends. The two approaches differ in the way such extrapolations are made and such resistances are estimated.

The former, in fact, identifies R with R_{AC} , measured by switching directions of the injected current [5] at some frequency f_{AC} , assumed high enough to avoid the onset of thermal effects in the device. No extrapolation is made. The latter instead, as shown in Fig. 8.1, which reports data for a device of the test group, finds R by extrapolation as the point of the real axis where the complex impedance porcupine diagram can be expected to finally land on it at very high frequency. The extrapolation is based on the a priori knowledge [3] that the "snout" of the porcupine slopes down at an asymptotic angle of 45° due to diffusion effects that are overlooked in the Harman approach.

Also shown in Fig. 8.1 is the electrical impedance z_{elAC} measured at 12.5 Hz, which is equal to the f_{AC} value used in this work for the measurement of R_{AC} with the commercial Time Domain zT meter. Clearly $|z_{elAC}|$ is always greater than R, but R_{AC} is a different thing yet because it is not measured in sine wave regime. Further discussion on this point will be given in the next section.

In order to estimate the DC resistance value, instead, the Time Domain approach extrapolates to steady state the step response, by assuming that it is shaped like an

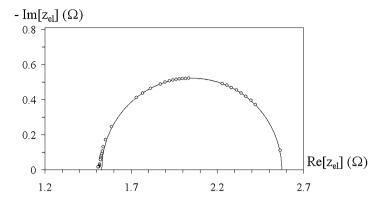


Fig. 8.2 Typical agreement between measured electrical impedance along the porcupine's body and the circle used to extrapolate it at low frequencies

asymptotic exponential [5], in order to identify an asymptotic voltage, and then divides the latter by the injected current. No provision is made for the possibility that diffusion effects may invalidate the assumption on the shape of the transient by making the lumped parameters model inadequate.

The Frequency Domain approach, in turn, extrapolates the porcupine impedance diagram down to very low frequencies, from the frequency range where it can be easily measured, on the assumption that it lays on a circle [3]. This procedure is valid in principle inasmuch as the lumped parameters model can be considered adequate down in that region. How valid it is in practice can be judged by inspection from the agreement shown in Fig. 8.2 between such extrapolating circle and the measured impedance points for one of the devices tested in this work. The result is typical.

Different optimization procedures can be devised to identify such circle from a limited number of experimental data, and one possible approach was illustrated in ref. 4. In the present work, the approach was taken to use a number of impedance data closely spaced in frequency in a range slightly above the thermal pole, and best fit to them a circle centered on the real axis. The DC resistance is then found as the resistance $R_{\rm C}$ of the circle center plus its radius *r*, as shown in Fig. 8.3.

The Type A uncertainty of results clearly depends on that associated with the individual impedance points used for the least square fit, which in turn depends on signal level (that is on injected current and number of pairs in the device) and on the number of averages chosen for the single data point. In the course of the evaluation of the modules considered in this work, which all had more than 60 pairs, an rms injected current of about 5 mA and averages of more than 20 samples were adequate to obtain statistical contributions to an uncertainty of the order of 0.5 % for zT and smaller yet for *R*.

Further comments will be given in the next section on the validity of the lumped parameters model and on extrapolations made in the two approaches in order to estimate the DC resistance.

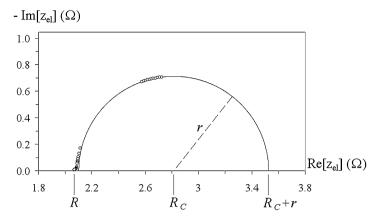


Fig. 8.3 Strategy used for the low frequency extrapolation based on a limited number of measured impedance points just above the thermal pole. The estimated circle center R_c and radius r are shown

Results and Discussions

Values of series ohmic resistance and figure of merit obtained with the two zT meters on four different devices at three different temperatures are reported in Table 8.1. All measurements were carried out in an environmental chamber with less than 0.3 K uncertainty, and enough time was allowed after changing temperature settings for reaching adequate uniformity in the chamber and inside the containers hosting the modules under test.

Series resistance results obtained with the porcupine meter are reported in Table 8.1 with 1 m Ω resolution because they are considered accurate better than 2 m Ω on the basis of the observed reproducibility (Type A contribution) and the absence of reasons to think that the adopted model is faulty at that level (Type B contribution). The reference resistor of the instrument [3, 4] is a 1 ppm/K Vishay[®] unit accurate to better than 10⁻⁴, which does not introduce uncertainty at the 1 m Ω level. Since a four terminal structure is used in this meter, the leads' resistance is not included. The most important cause of *R* result variability in porcupine measurements, incidentally, may well have been the 0.3 K instability of the chamber temperature, which is expected to introduce variations of about 0.15 % on the actual resistance value through the temperature coefficient, typically measured at the level of 0.5 %/K. All other results are reported in Table 8.1 with three significant digits.

Both zT and z results are reported for the RMT meter because, in spite of the fact that it actually measures zT, only z values are presented to the user, as calculated from zT by the embedded software. The ambient temperature T_a used for this is measured with a dedicated probe inside the sample holder. The z column shows therefore displayed experimental results, while data in the zT column are obtained by multiplying those by the measured T_a , as given by the meter itself. Type A uncertainties associated with quoted R and z results may well be dominated at the 1σ level

	Test	Harm	ian		Porcup	oine	Relative deviation	
Device trade name	temperature (°C)	$\overline{R_{ m AC}}$ (Ω)	z (1,000/K)	zT	$R(\Omega)$	zT	$\frac{\Delta R/R}{(\%)}$	$\Delta zT/zT$ (%)
Sirec TEC1-12704	20	1.56	2.42	0.709	1.460	0.707	+6.8	+0.3
	25	1.61	2.43	0.725	1.494	0.723	+7.8	+0.3
	30	1.64	2.43	0.737	1.531	0.737	+7.1	0.0
Sirec TEC1-12705	20	1.88	2.38	0.698	1.753	0.683	+7.2	+2.2
	25	1.94	2.36	0.704	1.800	0.693	+7.8	+1.6
	30	2.00	2.35	0.712	1.845	0.700	+8.4	+1.7
Sirec TEC1-12706	20	2.20	2.41	0.706	2.068	0.706	+6.4	0.0
	25	2.28	2.42	0.722	2.118	0.715	+7.6	+1.0
	30	2.36	2.41	0.731	2.174	0.725	+8.3	+1.2
RMT	20	1.03	2.21	0.648	0.933	0.634	+10.4	+2.2
1MDL06-050-03t	25	1.07	2.18	0.650	0.956	0.640	+11.9	+1.6
	30	1.09	2.19	0.664	0.982	0.645	+11.0	+2.8

Table 8.1 Results obtained with both meters for R and zT

Quoted zT values for the RMT meter are obtained by multiplying displayed z results times T_a . Relative deviations of R and zT are the Harman result minus the porcupine result divided by the latter. Shown discrepancies suggest the existence of undetected errors and Type B contributions as a consequence

of 5 m Ω for the resistance and of 5 × 10⁻⁶ for *z* by the second decimal digit truncation operated by the instrument. A trustable evaluation of Type B uncertainties appears much more difficult.

Uncertainties associated to results obtained with the porcupine meter were judged to be dominated by Type A contributions for both *R* and *zT*, at the level of less than 2 m Ω for the former and less than 0.004 for the latter. These estimates were based on repeatability of results in the presence of noise in impedance data. Uncertainties in radius and center of the porcupine body's approximating circle, whose estimate is needed for the calculation of uncertainty on *zT*, were determined with the well known sensitivity matrix technique in the context of the best fit least square routine. No evidence was found of model inadequacy at these levels.

Nevertheless, it can be noticed in looking at Table 8.1 that discrepancies exist, between ohmic resistance results obtained with the two methods, which are much greater than the quoted uncertainty, a clear sign that the used model is inadequate in at least one of the two approaches, leading to grossly underestimated Type B uncertainty.

Besides the irrelevant leads' resistance, which is included by the Harman meter, one cause for such discrepancy could certainly be thought to be the fact that the frequency at which R_{AC} is measured in the Harman meter is far from infinite, which in sine wave regime would lead to the operation point and the ohmic resistance evaluation error shown in Fig. 8.1. In fact, there is no reason why the meter should not measure R_{AC} in sine wave regime and reduce the error to the indicated level: in practice a fraction of the snout length, which in the case of Fig. 8.1 amounts to about 1 % on *R*. As it turns out, instead, the meter produces estimates of *R* which appear

	Harman		Porcupine			
Device trade name	$TC_R (mK)^{-1}$	$TC_{zT}(mK)^{-1}$	$TC_R (mK)^{-1}$	$TC_{zT} (mK)^{-1}$		
Sirec TEC1-12704	5.00 ± 0.20	3.9 ± 0.2	5.11 ± 0.08	4.2 ± 0.3		
Sirec TEC1-12705	6.20 ± 0.15	2.0 ± 0.2	5.11 ± 0.06	2.5 ± 0.2		
Sirec TEC1-12706	7.00 ± 0.15	3.5 ± 0.2	5.00 ± 0.05	2.7 ± 0.3		
RMT 1MDL06-050-03t	5.64 ± 0.30	2.4 ± 0.2	5.1 ± 0.1	1.7 ± 0.3		

Table 8.2 Results obtained with Harman and porcupine meters for the temperature coefficients (TC) of R and zT

Indicated uncertainties are Type A contributions only

to be biased by up to 12 % toward higher values for the tested devices, as shown in Table 8.1. Such a huge deviation appears to be probably caused by the step response of the device, which starts with an ideally infinite slope due to diffusion, so that no frequency is high enough to avoid thermal effects and allow to correctly isolate the ohmic voltage drop in the thermoelectric device if a square wave regime is adopted. A dedicated study would be needed to determine if this effect does indeed explain observed discrepancies, but this goes beyond the scope of this paper.

On the other hand, also the evaluation of the asymptotic value of the developed voltage that is made in the Harman approach is not immune from diffusion effects and may be altered by their existence. In fact, since the step response is not an asymptotic exponential, albeit less and less so as time elapses, a systematic error is generated when trying to estimate the asymptotic value by best fitting to experimental data a canonical RC type exponential response. Such an error is always positive, and its size depends on the time position along the response curve where the fit is attempted. Although this too needs closer consideration, it seems reasonable to think that errors incurred in this way by the Harman meter in the evaluation of the asymptotic voltage may just happen to be similar to the errors made in the evaluation of R, so that they roughly compensate them when zT is calculated from the ratio between asymptotic and AC developed voltages. It is suggested here that this might be the reason why zT values yielded by the two meters are so similar, while resistance results are instead so different. The relative deviation between R and zT evaluations obtained with the two meters is shown in percentage in Table 8.1 as the Harman result minus the porcupine result, divided by the latter.

The temperature coefficients (TC) of both *R* and *zT* are reported in Table 8.2 as calculated with a linear regression from results yielded by both meters. It can be noticed that, although in some cases they fail to agree within 2σ , TC estimates obtained with the two approaches are not substantially different, at least in the face of the huge discrepancy found in the estimate of series ohmic resistance. This fact can be taken as an indication that whatever systematic errors do exist in either method do not change significantly with temperature and are therefore mostly in common mode in slope calculations. However, it should be pointed out here that resistance TCs measured with the porcupine meter all turned out very close to one another for the tested devices, as one might expect from the fact that they all employ

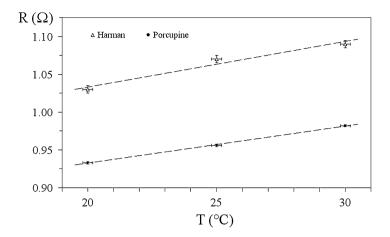


Fig. 8.4 Temperature dependence of *R* as estimated for the RMT module (model 1MDL06-050-03t) with the two instruments. Plotted uncertainty intervals are 1σ Type A contributions

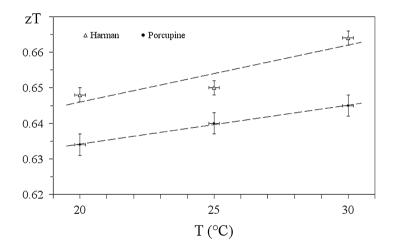


Fig. 8.5 Temperature dependence of zT as estimated for the RMT module (model 1MDL06-050-03t) with the two instruments. Plotted uncertainty intervals are 1σ Type A contributions

the same thermoelectric material (Bi_2Te_3) , while TC values measured with the Harman type meter do not; a clear indication that errors and Type B uncertainties are probably to be looked for in that part of the comparison.

In Figs. 8.4 and 8.5, a typical example of temperature dependence of R and zT is shown, as measured with the two meters on the RMT-1MDL06-050-03t module. It can be seen that the mean distance of data points from best fit regression straight lines is smaller than the indicated Type A uncertainty of data points themselves in the case of the porcupine meter, which suggests noise whiteness and lack of undetected systematic errors at the quoted level of uncertainty. In fact their variations

would likely show departure from whiteness it they existed. The same cannot be stated for temperature dependence plots of the Harman meter data, where the mean distance of data points from regression straight lines is greater than the indicated Type A uncertainty, suggesting the existence of Type B contributions.

Conclusions

In this paper, results obtained for the ohmic resistance R and the dimensionless figure of merit zT of a number of thermoelectric devices with a second generation prototype zT meter based on the porcupine method are compared with results obtained for the same devices by a commercial zT meter based on a variation of the Harman method. Each device was measured with both meters at three different temperatures in an environmental chamber. The ohmic resistance measured with the porcupine meter was consistently smaller than the value returned by the Harman meter, while figure of merit results were much more aligned. Type A uncertainties were estimated from the variability of measured data and their mean deviations from the linear regression line in plots of their temperature variations, and turned out to be typically <0.2 % for R and <0.5 % for zT with the porcupine meter, and about 0.5 % for R and <0.3 % for zT with the Harman type meter, limited in the latter case by truncation of displayed measurement results. Temperature coefficients of the series resistance were estimated with better than 2 and 5 % Type A uncertainty with the porcupine and the Harman meter respectively. Similarly, zT temperature coefficients were determined with Type A uncertainty of the order of 10 % with both meters. Disagreements between results obtained with the two methods for Rand zT could not be completely explained by published models, which is a clear sign that, at least in one of the two approaches, not all systematic errors have been detected yet, and residual Type B uncertainty contributions at the 10 % level should be considered to exist. It was argued that the model adopted in the Frequency Domain approach should be expected to grant accuracy at least at the percent level, and speculations were made on the directions in which further research should be done in order to compose such discrepancies.

References

- 1. Harman TC (1958) J Appl Phys 29:1373
- 2. Harman TC, Cahn JH, Logan MJ (1959) J Appl Phys 30:1351
- 3. De Marchi A, Giaretto V (2011) Rev Sci Instrum 82:034901. doi:10.1063/1.3558696
- 4. De Marchi A, Giaretto V, Caron S, Tona A (2013) J Electron Mater 42(9):2067. doi:10.1007/ s11664-013-2530-2
- Gromov G, Kondratiev D, Rogov A, Yershova L (2001) Proceedings of the 6th European workshop on thermoelectricity of the European Thermoelectric Society, Freiburg im Breisgau, p 1