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N n- ameti ic tati ical meth d , hich make fe e a m ti n ab t lati n e dit ib ti n , ha e e ha been nj tl neglect ed int he anal t ical cience . A maj ad ant age i t hat me f them a e im le t hat t he can be ed "at t he bench."

Pa amete n ameté ?

Anal ical scien is s generall make replica e meas remen s and rea hem as a random sample, from hich es ima es are made of he proper ies of he (h po he icall infini e) pop- la ion of meas remen s. The pop la ion mean, confidence limi s . are s all calc la ed sing he ass mp ion ha he nderl ing dis rib ion is normal (Ga ssian), i h mean μ and ariance σ^2, . . i can be s mmarised as $N(\mu,\sigma^2)$. The o erms μ and σ are he parame ers of he dis rib ion. Similarl a binomial dis rib ion is described as $B($, $)$, here he parame ers and are respec i el he o al n mber of meas remen s and he probabili of one of he o possible o comes.

This parame er-based approach o da a handling is no essen ial, and ma no al a s be appropria e. Some imes i is kno n ha a pop la ion dis rib ion is no normal or e en close o i , so ded c ions made on he ass mp ion of normali migh be nreliable. This is par ic larl r e in cases here he same meas remen s are made on similar b non-iden ical sample ma erials of na ral origin. The an ibod le els in blood plasma samples from differen h man s bjec s are ro ghl log-normall dis rib ed, i h he addi ion of some s bjec s i h e cep ionall high le els in ario s disease s a es. Me hods ha do no make ass mp ions abo he form of he pop la ion dis rib ion are called non-parame ric or dis rib ion-free me hods. In appl ing hem he familiar approach o significance es ing is s ill sed. We se p a n ll h po hesis H_0 and find he probabili of ob aining he ac al or more e reme res l s if H_0 is r e: if his probabili is er lo H_0 is rejec ed. B heir simplici makes non-parame ric me hods a rac i e e en in si a ions here more familiar es s s ch as he - es migh o her ise be applied, as he e amples belo ill sho .

S me im le e am le

S ppose ha an anal ical reagen is s a ed o ha e a p ri of 99.5%, and ha s ccessi e ba ches are fo nd o ha e p ri le els of 99.2%, 99.8%, 98.9%, 99.4%, 99.1%, 99.3%, and 99.0%. Is here e idence ha he p ri of he ma erial is lo er han i sho ld be? S ch res l s are nlikel o come from a normal pop la ion (after all, he ma im m possible p ri is 100%) so a - es or o her parame ric approach co ld ell be nsafe. A ke s a is ic here is he median: he n ll h po hesis is ha he da a come from a pop la ion i h a median p ri le el of 99.5%. To carr o he es e simpl s b rac his median from each of he e perimen al res l s, and no e he sign of he res l . This gi es si min s signs and one posi i e sign, . . si of he se en res l s lie belo he median. (An res l ha eq als he h po he ical median is ignored comple el). The probabili of ge ing si (or more) min s signs o of se en is pro ided b he binomial heorem, b he al es are pro ided in s a is ical ables, and can be memorised if e al a s make he same n mber of meas remen s. Here he probabili of ge ing 6 or more min s signs is 0.0625, a li le higher han he probabili le el commonl sed in significance es ing (= 0.05), so e re ain he n ll h po hesis ha he res l s co ld come from a pop la ion i h a median p ri of 99.5%. As al a s e ha e no pro ed ha he do come from s ch a pop la ion: e ha e

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failed o dispro e i . No e ha his is a one- ailed es , as he q es ion is he her he p ri , is lo er han i sho ld be. Wi h se en meas remen s he n ll h, po hesis o ld onl, be rejec ed a he = 0.05 le el if all se en res l s gi e min s signs hen compared i h he median al e: his o come has a probabili , of onl, $(1/2)^7 = 1/128$. This me hod is called he sign es , and i can be e ended o o her si a ions, s ch as comparing o se s of paired res l s, or s d, ing a possible rend in a seq ence of res l s.

Ano her simple es i h man, applica ions is called T ke, s Q ick Tes (after John W. T ke, , a major fig re in non-parame ric s a is ics and ini ial da a anal, sis) or he Tail Co n Tes , he la er being a good descrip ion of i s opera ion. I is sed o compare o independen da a se s, hich need no be of he same si e. S ppose e ob ain si al es of he le el of a mospheric NO (μg m^{-3}) a a roadside si e: 128, 121, 117, 125, 131 and 119. A a nearb, off-road si e e make si more meas remen s sing he same anal, ical me hod, ob aining he res l s 120, 108, 109, 112, 114 and 110 μg m^{-3}. Is here an, e idence ha he NO le el is lo er a he second si e han a he firs ? These o se s of res l s co ld be compared sing a (one- ailed) - es , b he T ke, approach is simpler. We simpl, co n he n mber of res l s in he firs da a se ha are higher han all he al es in he second se (here are 4 of hem), and he n mber of al es in he second se ha are lo er han all hose in he firs se (5 of hem). If ei her of hese co n s is ero, he es ends a once i h he n ll h, po hesis (here, ha mo ing a a, from he road does no affec he NO le el) being accep ed. O her ise he o co n s are added oge her o pro ide he es s a is ic T (= 9 here), and his is compared i h he cri ical al e. For a one- ailed es a = 0.05, T m s be grea er han or eq al o 6 if H_0 is o be rejec ed. So H_0 can be rejec ed here; he NO le el a he off-road si e does seem o be lo er. The meri of he T ke, me hod is ha if he o al n mber of meas remen s is no more han ~20, and if he o sample si es are no grea l, differen (condi ions often me in anal, ical prac ice), he cri ical T al es are independen of sample si e! For he rejec ion of he n ll h, po hesis in a one- ailed es he al e of T m s be ≥6, 7, 10 and 14 a = 0.05, 0.025, 0.005, and 0.0005 respec i el, . For a o- ailed es he corresponding cri ical al es of T are 7, 8, 11 and 15 respec i el, . This remarkable fea re of he me hod means ha i can be carried o sing men al ari hme ic onl, .

What n t t like?

Man, non-parame ric me hods ha e been de eloped, incl ding es s analogo s o he familiar - and F- es s, anal, sis of ariance, and calibra ion and regression me hods, b despi e heir prac ical meri s onl, a fe ha e fo nd fa o r in he anal, ical sciences. One possible reason for his is ha mos non-parame ric me hods need a sample of a leas 6 meas remen s. Ano her reason is he gro ing pop lari , of rob s me hods (AMCTB 6, 50), hich are ell s i ed o he common si a ion here he error dis rib ion is nimodal b no er, differen from Ga ssian. F r hermore i is e iden ha in he o e amples abo e he f ll n merical con en of he da a is no sed. In he sign es onl, he signs of he differences are co n ed, no heir magni de; and in he T ke, me hod he es s a is ic is again a co n ra her han an e ac re ec ion of he n merical res l s. We migh h s e pec ha non-parame ric me hods o ld be poorer han me hods ise